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(54) POLYBUTYLENE TEREPHTHALATE AND POLYBUTYLENE TEREPHTHALATE COMPOSITION

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a polybutylene terephthalate (PBT) excellent in color, resistance to hydrolysis, heat stability, transparency, and moldability, decreased in foreign matter, and capable of suitably used for a film, a monofilament, a fiber, an electrical and electronic part, an automotive part, etc., and to provide a composition of the same.

SOLUTION: This PBT contains titanium of which the amount is not more than 80 ppm as titanium atom, and has a carboxy end group concentration of 6.0–17.0 $\mu\text{eq/g}$ and an intrinsic viscosity of 0.65–0.87 dL/g. The PBT composition resistant to the hydrolysis contains the PBT (A) in an amount of 100 pts.wt., an epoxy compound (B) in an amount of 0.01–20 pts.wt., and a reinforcing filler (C) in an amount of 0–200 pts.wt.

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CLAIMS

[Claim(s)]

[Claim 1]

Polybutylene terephthalate characterized by containing titanium and for the amount being 80 ppm or less as a titanium atom, for end carboxyl group concentration being 6~17microeq/g, and intrinsic viscosity being 0.65~0.83 dL/g.

[Claim 2]

Polybutylene terephthalate according to claim 1 the amount of whose titanium is contained and is 50 ppm or less as a titanium atom.

[Claim 3]

Polybutylene terephthalate according to claim 1 or 2 whose end methoxycarbonyl group concentration is below 0.5microeq/g.

[Claim 4]

Polybutylene terephthalate given in any of claims 1~3 whose temperature fall crystallization temperature measured in 20 degrees C in temperature fall rate / min with the differential scanning calorimeter is 170~190 degrees C they are.

[Claim 5]

Polybutylene terephthalate given in any of claims 1~4 whose end vinyl group concentration is 0.1~10microeq/g they are.

[Claim 6]

Polybutylene terephthalate given in any of claims 1~5 whose solution Hayes at the time of dissolving polybutylene terephthalate 2.7g in a phenol / tetrachloroethane mixed solvent (weight ratios 3/2) 20mL, and measuring is 10% or less they are.

[Claim 7]

Polybutylene terephthalate given in any of claims 1~6 whose lifting of the end carboxyl group concentration except the hydrolysis reaction at the time of heat-treating for 40 minutes at 245 degrees C under an inert gas ambient atmosphere is 0.1~30microeq/g they are.

[Claim 8]

Polybutylene terephthalate given in any of claims 1~7 whose foreign matters 5 micrometers or more are below 50 piece / 10g polymer they are.

[Claim 9]

a claim — one — eight — any — or — a publication — polybutylene terephthalate — (— A —) — 100 — weight — the section — receiving — an epoxy compound — (— B —) — 0.01 — 20 — weight — the section — a consolidation — a bulking agent — (— C —) — zero — 200 — weight — the section — containing — things — the description — ** — carrying out — “proof” — hydrolysis — a sex — polybutylene terephthalate — a constituent .

[Claim 10]

a claim — one — eight — any — or — a publication — polybutylene terephthalate — (— A —) — 100 — weight — the section — receiving — an epoxy compound — (— B —) — 0.01 — 20 — weight — the section — and — a shock resistant — amelioration — material — (— D —) — 0.5 — 40 — weight — the section — and — a consolidation — a bulking agent — (— C —) — zero — 200 — weight — the section — containing — things — the description — ** — carrying

out — shock resistance — polybutylene terephthalate — a constituent .

[Claim 11]

a claim — one — eight — any — or — a publication — polybutylene terephthalate — (— A —) — 100 — weight — the section — receiving — bromination — an aromatic compound — a system — a flame retarder — (— E —) — three — 50 — weight — the section — an antimony compound — (— F —) — one — 30 — weight — the section — dropping — an inhibitor — (— G —) — zero — 15 — weight — the section — and — a consolidation — a filler — (— C —) — zero — 200 — weight — the section — containing — things — the description — ** — carrying out — fire retardancy — polybutylene terephthalate — a constituent — .

[Claim 12]

a claim — one — eight — any — or — a publication — polybutylene terephthalate — (— A —) — 50 — 95 — weight — the section — polyphenylene ether — resin — (— H —) — five — 50 — weight — the section — a total — 100 — weight — the section — receiving — at least one sort of (Compound J) 2~45 chosen from a compatibilizer (I) 0.05 ~ 10 weight sections, phosphoric ester, or phospho nitril — weight — the section — a consolidation — a filler — (— C —) — zero — 200 — weight — the section — dropping — an inhibitor — (— G —) — zero — 15 — weight — the section — cyanuric acid — a melamine — (— K —) — zero — 45 — weight — the section — and — boric acid — a metal — a salt — (— L —) — zero — 50 — weight — the section — containing — things — the description — ** — carrying out — un — a halogen — fire retardancy — polybutylene terephthalate — a constituent .

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[Field of the Invention]

[0001]

This invention relates to the polybutylene terephthalate constituent which is excellent in a color tone, hydrolysis-proof nature, thermal stability, transparency, and a moldability, and moreover contains in detail the polybutylene terephthalate with which the foreign matter was reduced, and which can be used suitable for a film, a monofilament, fiber, electric electronic parts, autoparts, etc., and the polybutylene terephthalate concerned about polybutylene terephthalate and a polybutylene terephthalate constituent, and has various functions.

[Background of the Invention]

[0002]

That the ease of a fabricating operation, mechanical physical properties, thermal resistance, chemical resistance, a smell retaining property, and others are physical, and since it excels in chemical property, the polybutylene terephthalate which is engineering plastics typical in thermoplastic polyester resin is widely used for injection molding articles, such as autoparts, the electrical and electric equipment and electronic parts, and a precision machine vessel part article. In recent years, taking advantage of the outstanding property, it has come to be widely used also in fields, such as a film, a sheet, a monofilament, and fiber.

[0003]

Generally, it is known that hydrolysis-proof nature will get worse, so that end carboxyl group concentration is high (for example, nonpatent literature 1), also in polybutylene terephthalate, the hydrolysis reaction rate of polyester under wet heat is so large that end carboxyl group concentration is high, and it is a big problem to cause the molecular weight lowering by hydrolysis, as a result lowering of mechanical physical properties etc.

[0004]

In order to solve the above-mentioned problem, reducing end carboxyl group concentration is widely performed by once solidifying the polybutylene terephthalate obtained by the melting polymerization, and carrying out solid state polymerization at the temperature below the melting point (example, patent reference 1 reference).

[0005]

However, performing solid state polymerization after a melting polymerization means that a process increases, and it has a problem in respect of the complicatedness of actuation by it, aggravation of productivity, etc.

[0006]

Moreover, with the conventional polybutylene terephthalate, since the usual melting shaping is performed above the melting point of polybutylene terephthalate, even if it reduces end carboxyl group concentration by solid state polymerization, when lifting of end carboxyl group concentration takes place again at the time of molding and it becomes a product after shaping, there is a problem that the effectiveness of solid state polymerization will become small.

[0007]

On the other hand, especially, for applications, such as a film, a sheet, a monofilament, and fiber.

[0015]

This invention -- the -- three -- a summary -- the -- one -- a summary -- starting -- polybutylene terephthalate -- (A) -- 100 -- weight -- the section -- receiving -- an epoxy compound -- (B) -- 0.01 -- 20 -- weight -- the section -- a shock resistant -- amelioration -- material -- (D) -- 0.5 -- 40 -- weight -- the section -- and -- a consolidation -- a bulking agent -- (C) -- zero -- 200 -- weight -- the section -- containing -- things -- the description -- ** -- carrying out -- shock resistance -- polybutylene terephthalate -- a constituent -- consisting .

[0016]

This invention -- the -- four -- a summary -- the -- one -- a summary -- starting -- polybutylene terephthalate -- (A) -- 100 -- weight -- the section -- receiving -- bromination -- an aromatic compound -- a system -- a flame retarder -- (E) -- three -- 50 -- weight -- the section -- an antimony compound -- (F) -- one -- 30 -- weight -- the section -- dropping -- an inhibitor -- (G) -- zero -- 15 -- weight -- the section -- and -- a consolidation -- a filler -- (C) -- zero -- 200 -- weight -- the section -- containing -- things -- the description -- ** -- carrying out -- fire retardancy -- polybutylene terephthalate -- a constituent -- consisting .

[0017]

This invention -- the -- five -- a summary -- the -- one -- a summary -- starting -- polybutylene terephthalate -- (A) -- 50 -- 95 -- weight -- the section -- polyphenylene ether -- resin -- (H) -- five -- 50 -- weight -- the section -- a total -- 100 -- weight -- the section -- receiving -- at least one sort of (Compound J) 2--45 chosen from a compatibilizer (I) 0.05 -- 10 weight sections, phosphoric ester, or phospho nitril -- weight -- the section -- a consolidation -- a filler -- (C) -- zero -- 200 -- weight -- the section -- dropping -- an inhibitor -- (G) -- zero -- 15 -- weight -- the section -- cyanuric acid -- a melamine -- (K) -- zero -- 45 -- weight -- the section -- and -- boric acid -- a metal -- a salt -- (L) -- zero -- 50 -- weight -- the section -- containing -- things -- the description -- ** -- carrying out -- un -- a halogen -- fire retardancy -- polybutylene terephthalate -- a constituent -- consisting .

[Effect of the Invention]

[0018]

According to this invention, it excels in a color tone, hydrolysis-proof nature, thermal stability, transparency, and a moldability, and, moreover, the polybutylene terephthalate with which the foreign matter was reduced and which can be used suitable for a film, a monofilament, fiber, electric electronic parts, autoparts, etc., and its constituent are offered.

[Best Mode of Carrying Out the Invention]

[0019]

<Polybutylene terephthalate>

Hereafter, this invention is explained to a detail. The polybutylene terephthalate (it is hereafter written as PBT) of this invention says the macromolecule with which it has the structure in which the terephthalic-acid unit and the 1,4-butanediol unit carried out the ester bond, more than 50 mol % of a dicarboxylic acid unit consists of a terephthalic-acid unit, and more than 50 mol % of a diol unit consists of a 1,4-butanediol unit. the rate of the terephthalic-acid unit in [all] a dicarboxylic acid unit -- desirable -- more than 70 mol % -- further -- desirable -- more than 80 mol % -- especially -- desirable -- more than 95 mol % -- it -- the rate of the 1,4-butanediol unit [all] a diol unit -- desirable -- more than 70 mol % -- further -- desirable -- more than 80 mol % -- it is more than 95 mol % especially preferably. When there are few terephthalic-acid units or 1,4-butanediol units than 50 mol %, the crystallization rate of PBT falls and aggravation of a moldability is caused.

[0020]

In this invention, there is especially no limit in dicarboxylic acid components other than a terephthalic acid. For example, phthalic-acid, isophthalic acid, 4, and 4'-diphenyl dicarboxylic acid, - diphenyl ether dicarboxylic acid, and 4 and 4', 4''-benzophenone dicarboxylic acid, - difenoxydicarboxylic acid, and 4 and 4', 4''-diphenylsulfone dicarboxylic acid, Aromatic series

since commodity value is greatly influenced by a foreign matter, Hayes, coloring, etc., these reduction and amelioration are called for strongly. The deactivation matter and condensation matter of metallic compounds which add the foreign matter and Hayes in polybutylene terephthalate as a catalyst besides the degradation object of the resin generally called YAKE and a discharge from the eyes are considered to be the cause.

[0008]

Then, the reaction which esterifies a terephthalic acid and 1,4-butanediol continuously is divided into two steps, in the 1st-step esterification reaction, only an organotin compound is added, an organic titanium compound is added by the 2nd-step esterification reaction, and the method of reducing the foreign matter of the catalyst origin and Hayes is proposed (for example, patent reference 2 reference).

[0009]

However, there is a problem of a foreign matter and the reduction effectiveness of Hayes being restrictive, and causing aggravation and heat-resistant aggravation of the polymer color tone by these metallic compounds, for the catalyst which remains in polybutylene terephthalate also by the above-mentioned approach, or catalyst residue (patent reference 2 reference). Moreover, since it is accelerated according to a residual catalyst, lifting of the end carboxyl group concentration at the time of melting mentioned above also has the fault of causing aggravation of hydrolysis-proof nature as a result.

[0010]

[Nonpatent literature 1] Saturated polyester resin handbook (December 22, 1989, the Nikkan Kogyo Shinbun issuance, the 192--193rd page)

[Patent reference 1] JP,9-316183A

[Patent reference 2] JP,10-330468A

[Description of the Invention]

[Problem(s) to be Solved by the Invention]

[0011]

It is offering the polybutylene terephthalate constituent which contains the polybutylene terephthalate with which the object was excellent in a color tone, hydrolysis-proof nature, thermal stability, transparency, and a moldability with polybutylene terephthalate, and the foreign matter was moreover reduced, and which can be used suitable for a film, a monofilament, fiber, electric electronic parts, autoparts, etc., and the polybutylene terephthalate concerned by making this invention in view of the above-mentioned actual condition, and has various functions.

[Means for Solving the Problem]

[0012]

If this invention persons supplied the titanium catalyst and the raw material in the specific mode and performed the esterification reaction as a result of repeating research wholeheartedly that the above-mentioned technical problem should be solved, the utilization effectiveness of a titanium catalyst was raised to the surprising thing, the new polybutylene terephthalate end carboxyl group concentration and whose intrinsic viscosity are specific range was obtained, and, thereby, they resulted that the above-mentioned technical problem could be solved easily in completion of a header and this invention.

[0013]

This invention is completed based on the above-mentioned knowledge, and the 1st summary contains titanium, and the amount is 80 ppm or less as a titanium atom, and it consists in the polybutylene terephthalate characterized by for end carboxyl group concentration being 6--17microeq/g, and intrinsic viscosity being 0.65 -- 0.83 dL/g.

[0014]

this invention -- the -- two -- a summary -- polybutylene terephthalate -- (A) -- 100 -- weight -- the section -- receiving -- an epoxy compound -- (B) -- 0.01 -- 20 -- weight -- the section -- and -- a consolidation -- a bulking agent -- (C) -- zero -- 200 -- weight -- the section -- containing -- things -- the description -- ** -- carrying out -- --proof -- hydrolysis -- a sex -- polybutylene terephthalate -- a constituent -- consisting .

dicarboxylic acid, such as 2 and 6-naphthalene dicarboxylic acid, 1,2-cyclohexane dicarboxylic acid, Aliphatic series dicarboxylic acid, such as alicyclic dicarboxylic acid, such as 1,3-cyclohexane dicarboxylic acid, 1, and 4-cyclohexane dicarboxylic acid, a malonic acid, a succinic acid, a glutaric acid, an adipic acid, a pimelic acid, a suberic acid, an azelaic acid, and a sebacic acid, etc. can be mentioned. These dicarboxylic acid components can be introduced into a polymer frame by using dicarboxylic acid derivatives, such as dicarboxylic acid ester as dicarboxylic acid, and dicarboxylic acid halide, as a raw material.

[0021]

In this invention, there is especially no limit in diol components other than 1,4-butanediol. For example, ethylene glycol, a diethylene glycol, a polyethylene glycol, 1,2-propanediol, 1,3-propanediol, a propylene glycol, a polypropylene glycol, a polytetramethylene glycol and a jib -- a CHIREN glycol and 1,5-pentanediol -- Aliphatic series diols, such as neopentyl glycol, 1,6-hexanediol, 1, and 8-octanediol, 1,2-cyclohexane diol, 1,4-cyclohexane diol, Aromatic series diols, such as 1 and 1-cyclohexane dimethylol, 1, and 4-cyclohexane dimethylol, Aromatic series diols, such as a xylylene glycol, 4, and 4'-dihydroxy biphenyl, 2, and 2-bis(4-hydroxyphenyl) propane and a bis(4-hydroxyphenyl) sulfone, etc. can be mentioned.

[0022]

In this invention further A lactic acid, a glycolic acid, m-hydroxybenzoic acid, Para hydroxybenzoic acid, a β-hydroxy-2-naphthalene carboxylic acid, Hydroxycarboxylic acid, such as a β-beta-hydroxy ethoxy benzoic acid, An alkoxy carboxylic acid, stearyl alcohol, benzyl alcohol, Monofunctional components, such as stearin acid, a benzoic acid, t-butyl benzoic acid, and benzoylbenzoic acid. Polyfunctional components of three or more organic functions, such as tricarboxylic acid, trimellitic acid, trimellitic acid, trimellitic acid, pyromellitic acid, a gallic acid, trimethylol propane, glycerol, and pentaerythritol, etc. can be used as a copolymerization component.

[0023]

PBT of this invention is obtained as a catalyst using a titanium catalyst in the case of the esterification reaction (or ester exchange reaction) of 1,4-butanediol and a terephthalic acid (or terephthalic-acid dialkyl).

[0024]

As a titanium catalyst, a titanium compound is used and titanium phenolates, such as titanium alcohols, such as inorganic titanium compounds, such as titanium oxide and a titanium tetrachloride, tetramethyl titanate, tetra-isopropyl titanate, and tetra-butyl titanate, and tetra-phenyl titanate, etc. are usually mentioned as the example. In these, tetra-alkyl titanate is desirable, and tetra-butyl titanate is desirable in it.

[0025]

The tin other than titanium may be used as a catalyst. Tin is usually used as a tin compound. As the example Dibutyltin oxide, methylphenyl tin oxide, tetraethyltin, Hexa ethyl JISUZU oxide, cyclohexa hexyl JISUZU oxide, Dodecetyl oxide, triethyl tin hydroxide, triphenyltin hydroxide, TORISO butyl tin acetate, dibutyltin diacetate, diphenyl SUZUJI laurate, Monobutyltin trichloride, tributyltin chloride, dibutyltin sulfide, butyl hydroxy tin oxide, a MECHIRUSU tongue non acid, ethylstannane acid, a BUCHIRUSU tongue non acid, etc. are mentioned.

[0026]

Besides titanium, moreover, magnesium acetate, a magnesium hydroxide, a magnesium carbonate, Magnesium compounds, such as a magnesium oxide, magnesium alkoxide, and phosphoric acid hydrogen magnesium, Calcium acetate, a calcium hydroxide, a calcium carbonate, a calcium oxide, Others [lime compounds], such as calcium alkoxide and calcium hydrogen phosphate], Germanium compounds, such as antimony compounds, such as an antimony trioxide, diacid-ized germanium, and 4 germanium dioxides, Reaction assistants, such as phosphorus compounds, such as a manganese compound, a zinc compound, a zirconium compound, a cobalt compound, orthophosphoric acid, phosphorous acid, hypophosphorous acid, polyphosphoric acid, those ester, and a metal salt, a sodium hydroxide, and sodium benzoate, may be used.

[0027]

An aforementioned catalyst and an aforementioned reaction assistant may be *****ed in the phase of the polycondensation reaction which may carry out division addition when an esterification reaction (or ester exchange reaction) consists of two or more tubs, and continues. [0028]

PBT of this invention contains titanium and is characterized by the amount being 80 ppm or less as a titanium atom. The above-mentioned value is an atomic weight ratio to PBT. [0029]

In this invention, 3 ppm of 5 ppm of 8 ppm of minimums of the above-mentioned titanium content are 1 ppm usually 15 ppm much more preferably especially preferably still more preferably preferably. 70 ppm of 50 ppm of 40 ppm of upper limits of a titanium content are 33 ppm much more preferably especially preferably still more preferably preferably. When there are more contents of titanium than 80 ppm, a color tone, hydrolysis-proof nature, transparency, a moldability, etc. get worse, moreover it is in the inclination which a foreign matter also increases, and when fewer than 1 ppm, polymerization nature may get worse. [0030]

In this invention, a tin catalyst can be used with a titanium catalyst as above-mentioned. Generally, since catalyst ability is low compared with a titanium catalyst, a tin catalyst needs to make [many] an addition compared with a titanium catalyst. However, when there is too much amount of the tin catalyst used, aggravation of a color tone is caused and, moreover, tin is toxic. Therefore, it is 20 ppm or less still more preferably, and the 50 ppm or less of the 100 ppm or less of the amount of the tin catalyst used are usually that the most desirable mode does not use a tin catalyst preferably. The content of a titanium atom etc. is atom luminescence after collecting the metals in a polymer by approaches, such as a wet ashing, atomic absorption, and induced. Coupled it can measure using approaches, such as Plasma (ICP). [0031]

The intrinsic viscosity of PBT of this invention needs to be 0.65 ~ 0.83 dL/g, and is 0.68 ~ 0.75 dL/g still more preferably 0.68 to 0.80 dL/g preferably. When intrinsic viscosity is less than 0.65 dL/g, the mechanical strength of mold goods becomes inadequate, when exceeding 0.83 dL/g, melt viscosity becomes high, a fluidity gets worse, and it is in the inclination for the end vinyl group which a moldability not only gets worse, but a color tone gets worse and it mentions later to also go up. The above-mentioned intrinsic viscosity is the value which used the mixed solvent of a phenol/tetrachloroethane (weight ratios 1/1), and was measured at 30 degrees C. [0032]

the end carboxyl group concentration of PBT of this invention is 6~17microeq/g --- required --- desirable --- 6~12microeq/g --- further --- desirable --- 8~10microeq/g --- it considers as 7~9microeq/g preferably especially. When end carboxyl group concentration is too high, the hydrolysis-proof nature of PBT gets worse, and when too low, it is in the inclination for reactivity with finishing agents, such as a reactant additive which has functional groups, such as an epoxy group, a compatibilizer, and glass fiber, to fall, and for reinforcement, compatibility with other resin, etc. to fall at the time of a compound. [0033]

Moreover, if it goes up with the heat at the time of kneading and molding even if it lowers the end carboxyl group concentration of PBT, it not only worsens the hydrolysis-proof nature of a product as a result, but it will cause generating of gas, such as a tetrahydrofuran, therefore, lifting of the end carboxyl group concentration except the hydrolysis reaction at the time of heat-treating for 40 minutes at 245 degrees C under inert gas ambient atmospheres, such as nitrogen, helium, and an argon, --- usually --- 0.1~30microeq/g --- it is preferably good 0.1~10microeq/g and to consider as 2~8microeq/g still more preferably. A small inclination has lifting of the end carboxyl group concentration at the time of generally the one where molecular weight is higher applying [the direction / the content of the catalyst matter is low] heat. [0034]

Having specified temperature and time amount in the above-mentioned appraisal method has the too small rate of lifting of end carboxyl group concentration, when time amount is too short in temperature being too low, and when it is reverse, it is because it is too large and assessment

signal, pole little addition of the basic components, such as a heavy pyridine, etc. may be carried out. [0042]

170~200 degrees C of 170~190 degrees C of 172~185 degrees C of temperature fall crystallization temperature of PBT of this invention are usually especially made into 175~180 degrees C preferably still more preferably. The temperature fall crystallization temperature in this invention is the temperature of the exothermic peak by crystallization which appears when it cools by 20 degrees C in temperature fall rate / min from the condition which resin fused using the differential scanning calorimeter. Temperature fall crystallization temperature corresponds with a crystallization rate, since the crystallization rate is quick, can shorten a cooldown delay on the occasion of injection molding, and can raise productivity, so that temperature fall crystallization temperature is high. When temperature fall crystallization temperature is low, on the occasion of injection molding, crystallization takes time amount, and it is in the inclination to lengthen the cooldown delay after injection molding, for a molding cycle to be extended, and for productivity to fall. [0043]

Although especially solution Hayes of PBT of this invention is not restricted, it is usually especially made into 1% or less preferably 3% or less still more preferably 5% or less 10% or less as solution Hayes at the time of dissolving PBT:7g in a phenol / tetrachloroethane, mixed solvent (weight ratios 3/2) 20mL, and measuring. When solution Hayes is high, transparency gets worse, and since there is an inclination which a foreign matter also increases, a film, a monofilament, fiber, etc. lower commodity value remarkably in the application as which especially transparency is required. Solution Hayes has many catalyst contents, or has the inclination to go up when deactivation of a catalyst is large. [0044]

Moreover, a foreign matter with a die length of 5 micrometers or more contained in PBT of this invention is usually made into below 80 piece / 10g polymer. In the application for which the foreign matter in raw material PBT resin, such as a film and a monofilament, influences product quality greatly especially, 50 or less pieces are especially made into 30 or less pieces preferably 40 or less pieces still more preferably. [0045]

After the above-mentioned amount of foreign matters dissolving PBT10g in the mixed solvent of hexafluoro isopropanol / chloroform = 2 / 3 (volume ratio) by 20% of the weight of concentration and filtering it with the membrane filter made from polytetrafluoroethylene of 5 micrometers of apertures, the mixed solvent concerned can wash it enough and it can be calculated by the approach of observing and carrying out counting of the amount of foreign matters (number) which remained on the filter with an optical microscope. [0046]

Next, the manufacture approach of PBT of this invention is explained. The manufacture approach of PBT is divided roughly into the so-called direct polymerization method which uses dicarboxylic acid as a main raw material, and the ester interchange method which uses dicarboxylic acid dialkyl as a main raw material from a raw material side. Water generates the former by the early esterification reaction, and the latter has a difference that alcohol generates by the early ester exchange reaction. [0047]

Moreover, the manufacture approach of PBT of this invention is divided roughly into a batch process and a continuous magnetization method from feeding or the expenditure gestalt of a polymer. There is also a method of performing an early esterification reaction or an early ester exchange reaction by consecutive operation, and performing the polycondensation following it by batch operation, or carrying out an early esterification reaction or an early ester exchange reaction to reverse by batch operation, and performing the polycondensation following it by consecutive operation. [0048]

In this invention, the viewpoint of the amelioration effectiveness by the acquisition stability of a raw material, the ease of processing of a distillate, the height of a raw material material unit, and

becomes incorrectness. Moreover, when extremely high temperature estimates, it is also one of the reasons that the side reaction except an end carboxyl group generating occurs at the same time, and assessment becomes incorrectness. Lowering of the number average molecular weight by reactions other than the hydrolysis reaction which the moisture contained in PBT triggers on these heat treatment conditions can be ignored. A gone up part of the end carboxyl group concentration by the hydrolysis reaction Since it can consider that it is almost the same as a gone up part of the end hydroxyl-group concentration before and behind heat treatment, it can ask for a gone up part of the end carboxyl group concentration by pyrolysis reactions other than the hydrolysis reaction which poses a problem at the time of kneading and molding by the following formulas (1). [0035] [Equation 1]

$$\Delta AV(d) = \Delta AV(t) - \Delta AV(h) = \Delta AV(i) - \Delta OH \quad (1)$$

Here, the variation of the end carboxyl group concentration according [deltaAV(d)] to a pyrolysis reaction, the variation of the end carboxyl group concentration according [all the variation of the end carboxyl group concentration before and behind heat treatment and deltaAV(h)] to a hydrolysis reaction in deltaAV(t), and deltaOH express the variation of the end hydroxyl-group concentration before and behind heat treatment.

Since the direction with few hydrolysis reactions from a viewpoint of the dependability of pyrolysis reaction assessment is desirable, as for the moisture content of PBT used for heat treatment, 300 ppm or less are usually recommended. The quantum of the end hydroxyl-group concentration before and behind heat treatment can be carried out by 1 H-NMR.

The end carboxyl group concentration of PBT can dissolve PBT in an organic solvent etc., and can calculate it by titrating using alkali solutions, such as a sodium-hydroxide solution.

moreover, the end vinyl group concentration of PBT of this invention --- usually --- 0.1~10microeq/g --- desirable --- 0.5~5microeq/g --- it considers as 1~4microeq/g still more preferably. When end vinyl group concentration is too high, it becomes the cause of color tone aggravation or solid-state-polymerization nature aggravation. Since raising polymerization temperature generally or lengthening reaction time is called for without reducing productivity when PBT with large molecular weight and PBT with low catalyst concentration tend to be manufactured, end vinyl group concentration tends to rise. End vinyl group concentration can dissolve PBT in heavy chloroform / hexafluoro isopropanol = 7 / 3 (volume ratio), and can carry out a quantum by measuring 1 H-NMR.

At the end of PBT, when the methoxycarbonyl group of the raw material origin may remain in everything but a hydroxyl group, a carboxyl group, and a vinyl group and it uses dimethyl terephthalate as a raw material especially at it, it may remain mostly. By the way, these toxicity becomes a problem, when a methoxycarbonyl end generates a methanol, formaldehyde, and formic acid and is especially used for a food-grade way by the heat by solid state polymerization, kneading, molding, etc. Moreover, formic acid damages a metal making machine machine, a metal vacuum related equipment, etc. Then, end methoxycarbonyl group concentration in this invention is usually especially made below into 0.1microeq/g preferably below 0.2microeq/g still more preferably below 0.3microeq/g below 0.5microeq/g.

Each above-mentioned end group concentration can dissolve PBT in the mixed solvent of heavy chloroform / hexafluoro isopropanol = 7 / 3 (volume ratio), and can carry out a quantum by measuring 1 H-NMR. Under the present circumstances, in order to prevent a lap with a solvent

signal, pole little addition of the basic components, such as a heavy pyridine, etc. may be carried out. [0042]

170~200 degrees C of 170~190 degrees C of 172~185 degrees C of temperature fall crystallization temperature of PBT of this invention are usually especially made into 175~180 degrees C preferably still more preferably. The temperature fall crystallization temperature in this invention is the temperature of the exothermic peak by crystallization which appears when it cools by 20 degrees C in temperature fall rate / min from the condition which resin fused using the differential scanning calorimeter. Temperature fall crystallization temperature corresponds with a crystallization rate, since the crystallization rate is quick, can shorten a cooldown delay on the occasion of injection molding, and can raise productivity, so that temperature fall crystallization temperature is high. When temperature fall crystallization temperature is low, on the occasion of injection molding, crystallization takes time amount, and it is in the inclination to lengthen the cooldown delay after injection molding, for a molding cycle to be extended, and for productivity to fall. [0043]

Although especially solution Hayes of PBT of this invention is not restricted, it is usually especially made into 1% or less preferably 3% or less still more preferably 5% or less 10% or less as solution Hayes at the time of dissolving PBT:7g in a phenol / tetrachloroethane, mixed solvent (weight ratios 3/2) 20mL, and measuring. When solution Hayes is high, transparency gets worse, and since there is an inclination which a foreign matter also increases, a film, a monofilament, fiber, etc. lower commodity value remarkably in the application as which especially transparency is required. Solution Hayes has many catalyst contents, or has the inclination to go up when deactivation of a catalyst is large. [0044]

Moreover, a foreign matter with a die length of 5 micrometers or more contained in PBT of this invention is usually made into below 80 piece / 10g polymer. In the application for which the foreign matter in raw material PBT resin, such as a film and a monofilament, influences product quality greatly especially, 50 or less pieces are especially made into 30 or less pieces preferably 40 or less pieces still more preferably. [0045]

After the above-mentioned amount of foreign matters dissolving PBT10g in the mixed solvent of hexafluoro isopropanol / chloroform = 2 / 3 (volume ratio) by 20% of the weight of concentration and filtering it with the membrane filter made from polytetrafluoroethylene of 5 micrometers of apertures, the mixed solvent concerned can wash it enough and it can be calculated by the approach of observing and carrying out counting of the amount of foreign matters (number) which remained on the filter with an optical microscope. [0046]

Next, the manufacture approach of PBT of this invention is explained. The manufacture approach of PBT is divided roughly into the so-called direct polymerization method which uses dicarboxylic acid as a main raw material, and the ester interchange method which uses dicarboxylic acid dialkyl as a main raw material from a raw material side. Water generates the former by the early esterification reaction, and the latter has a difference that alcohol generates by the early ester exchange reaction. [0047]

Moreover, the manufacture approach of PBT of this invention is divided roughly into a batch process and a continuous magnetization method from feeding or the expenditure gestalt of a polymer. There is also a method of performing an early esterification reaction or an early ester exchange reaction by consecutive operation, and performing the polycondensation following it by batch operation, or carrying out an early esterification reaction or an early ester exchange reaction to reverse by batch operation, and performing the polycondensation following it by consecutive operation. [0048]

In this invention, the viewpoint of the amelioration effectiveness by the acquisition stability of a raw material, the ease of processing of a distillate, the height of a raw material material unit, and

this invention to a direct polymerization method is desirable. Moreover, in this invention, from productivity, the stability of product quality, and a viewpoint of the amelioration effectiveness by this invention, a raw material is supplied continuously and the approach of performing an esterification reaction or an ester exchange reaction continuously is adopted. And in this invention, the so-called continuous magnetization method which also performs continuously the polycondensation reaction following an esterification reaction or an ester exchange reaction is desirable.

In this invention, the process which esterifies continuously a terephthalic acid (or terephthalic-acid dialkyl) and 1,4-butanediol (or ester interchange) is adopted preferably, supplying a part of [at least] 1,4-butanediol to an esterification reaction vessel (or ester exchange reaction tub) independently of a terephthalic acid (or terephthalic-acid dialkyl) under existence of a titanium catalyst in an esterification reaction vessel (or ester exchange reaction tub).

That is, in this invention, in order to reduce Hayes and the foreign matter originating in a catalyst and not to reduce catalytic activity, another moreover, 1,4-butanediol is supplied to an esterification reaction vessel or an ester exchange reaction tub independently of a terephthalic acid or terephthalic-acid dialkyl as a raw material slurry to a solution with the 1,4-butanediol supplied with a terephthalic acid or terephthalic-acid dialkyl ester. Henceforth; the 1,4-butanediol concerned may be called "another supply 1,4-butanediol."

Fresh 1,4-butanediol unrelated to a process can be applied to the above-mentioned "another supply 1,4-butanediol." Moreover, "another supply 1,4-butanediol" carries out uptake of the 1,4-butanediol distilled from the esterification reaction vessel or the ester exchange reaction tub by a capacitor etc., and it can be held to a tank etc. as it is or temporarily, and a reaction vessel can be made to be able to flow back or it can also supply it as 1,4-butanediol which separated and refined the impurity and raised purity. Henceforth, "another supply 1,4-butanediol" which consists of 1,4-butanediol by which uptake was carried out by the capacitor etc. may be called "recirculation 1,4-butanediol." It is desirable to apply "recirculation 1,4-butanediol" to "another supply 1,4-butanediol" from a viewpoint of effective use of a resource and the simplicity of a facility.

Moreover, the 1,4-butanediol distilled from the esterification reaction vessel or the ester exchange reaction tub usually contains components, such as water, alcohol, a tetrahydrofuran, and dihydrofuran, in addition to the 1,4-butanediol component. Therefore, as for the above-mentioned 1,4-butanediol which carried out the distillate, it is desirable to dissociate [components, such as water, alcohol, and a tetrahydrofuran, and], to refine and to return to a reaction vessel, carrying out uptake, after carrying out uptake by a capacitor etc.

And in this invention, it is desirable to return 10 % of the weight or more in "another supply 1,4-butanediol" to the reaction mixture liquid phase section directly. Here, the reaction mixture liquid phase section shows the liquid phase side of the gas-liquid interface in an esterification reaction vessel or an ester exchange reaction tub, and means that a direct liquid phase part is supplied without "another supply 1,4-butanediol" going returning to the reaction mixture liquid phase section directly via the gaseous-phase section using piping etc. The rate directly returned to the reaction mixture liquid phase section is 90 % of the weight or more most preferably 80% of the weight or more especially preferably 50% of the weight or more still more preferably 30% of the weight or more. "Another supply 1,4-butanediol" of a foreign matter directly returned to the reaction mixture liquid phase section tends to increase, when few.

Moreover, 100~200 degrees C of temperature of "another supply 1,4-butanediol" at the time of returning to a reactor are 50~220 degrees C usually preferably made into 150~190 degrees C still more preferably. When the temperature of "another supply 1,4-butanediol" is too high, the amount of byproducts of a tetrahydrofuran tends to increase, and since thermal loads

increase in number when too low, there is an inclination which causes an energy loss.

[0055]

Moreover, in this invention, in order to reduce Hayes and the foreign matter originating in a catalyst and not to reduce catalytic activity, it is desirable to supply directly 10 % of the weight or more in the titanium catalyst used for an esterification reaction (or ester exchange reaction) to the reaction mixture liquid phase section independently of a terephthalic acid (or terephthalic-acid dialkyl). Here, the reaction mixture liquid phase section shows the liquid phase side of the gas-liquid interface in an esterification reaction vessel or an ester exchange reaction tub, uses piping etc. as supplying the reaction mixture liquid phase section directly, and means that a direct liquid phase part is supplied without a titanium catalyst going via the gaseous-phase section of a reactor. The rate of the titanium catalyst directly added in the reaction mixture liquid phase section is 90 % of the weight or more most preferably 80% of the weight or more especially preferably 50% of the weight or more still more preferably 30% of the weight or more.

[0056]

Although it can be made to be able to dissolve in a solvent etc. or the above-mentioned titanium catalyst can also be supplied to the reaction mixture liquid phase section of a direct esterification reaction vessel or an ester exchange reaction tub, without making it dissolve, in order to stabilize the amount of supply and to mitigate adverse effects, such as denaturation by the heat from the thermal jacket of a reactor etc., diluting with solvents, such as 1,4-butanediol, is desirable, as the concentration of a titanium catalyst [as opposed to the whole solution in the concentration in this case] -- usually -- still more preferably is preferably taken for 0.08 - 8 % of the weight 0.05 to 10% of the weight 0.01 to 20% of the weight. Moreover, moisture concentration in a solution is usually made into 0.05 - 1.0 % of the weight from a viewpoint of foreign matter reduction. 30-100 degrees C of temperature in the case of solution preparation are 20-150 degrees C usually preferably made into 40-80 degrees C still more preferably from a viewpoint which prevents deactivation and condensation. Moreover, as for a catalyst solution, it is desirable to mix with another supply 1,4-butanediol for piping etc., and to supply an esterification reaction vessel or an ester exchange reaction tub from the point of degradation prevention, deposit prevention, and foreign matter control.

[0057]

An example of the continuous magnetization method which adopted the direct polymerization method is as follows. Said diol component which uses as a principal component said dicarboxylic acid component to which a terephthalic acid is used as a principal component, and 1,4-butanediol is mixed by the raw material mixing chamber, and it considers as a slurry. Namely, within an unit or two or more esterification reaction vessels Under existence of a titanium catalyst, preferably 180-260 degrees C usually 200-245 degrees C, furthermore -- desirable -- the temperature of 210-235 degrees C -- moreover -- usually -- under the pressure of 60-90kPa still more preferably 13 to 101 kPa preferably ter to 133 kPa It is 1 - 6 hours preferably, an esterification reaction is carried out continuously for 0.5 to 10 hours, and the oligomer as an acquired esterification resultant is transported to a polycondensation reaction vessel. Usually, within an unit or two or more polycondensation reaction vessels Under existence of a polycondensation catalyst, still more preferably 20 or less kPas 210-280 degrees C continuously usually preferably the temperature of 220-265 degrees C, and 27 or less kPa usually under reduced pressure of 13 or less kPas Under stirring, a polycondensation reaction is usually carried out preferably in 2 - 5 hours for 2 to 10 hours. The polymer obtained by the polycondensation reaction is cut by the cutter after water cooling, while it is transported to a polymer draw die from the pars basilaris ossis occipitalis of a polycondensation reaction vessel, and is usually extruded in the shape of a strand and water cooling is carried out, and let them be granules, such as the shape of a pellet type and a chip.

[0058]

As for the mole ratio of a terephthalic acid and 1,4-butanediol, in the case of a direct polymerization method, it is desirable to fill the following formulas (II).

[0059]

[Equation 2]

1,4-butanediol supplied with a terephthalic acid or terephthalic-acid dialkyl ester as a raw material slurry or a solution, and 1,4-butanediol used as a solvent of a catalyst.

[0060]

As for an esterification reaction or an ester exchange reaction, in this invention, it is desirable to carry out at the temperature more than the boiling point of 1,4-butanediol because of reaction-time compaction. The boiling point of 1,4-butanediol is 205 degrees C in 101.1kPa (atmospheric pressure) in 230 degrees C and 50kPa, although it is dependent on the pressure of a reaction.

[0061]

a thing well-known as an esterification reaction vessel or an ester exchange reaction tub -- it can be used -- a vertical mold stirring complete-mixing tub, a vertical mold heat convection type mixing chamber, and a column -- it is good also as two or more tubs to which you may be which types, such as a type successive reaction tub, and the serial of congener or the tub of a different kind was carried out also as an unit tub. Especially the reaction vessel which has stirring equipment is desirable, and types which carry out a high-speed revolution, such as a turbine stator mold high-speed rotating type [besides / which consists of a power unit, bearing, a shaft, and a stirring aerofoil as stirring equipment / the usual type] agitator, a disc mill mold agitator, and a rotor mill mold agitator, can also be used.

[0070]

Especially the gestalt of stirring is not restricted, but can carry out a part of reaction mixture to the exterior of a reactor for piping besides the usual stirring approach which stirs the reaction mixture in a reaction vessel directly from the upper part of a reaction vessel, the lower part, the transverse part, etc., can stir it with a line mixer etc., and can also take the approach of circulating reaction mixture.

[0071]

The class of stirring aerofoil can choose a well-known thing, and, specifically, a propeller aerofoil, a screw aerofoil, a turbine blade, a fan turbine blade, a disk turbine blade, a FAUDORA aerofoil, a full zone aerofoil, the Max blend aerofoil, etc. are mentioned.

[0072]

In manufacture of PBT, usually two or more reaction vessels are used, the reaction vessel of 2-5 is used preferably, and molecular weight is raised one by one. Usually, it continues at an early esterification reaction or an early ester exchange reaction, and a polycondensation reaction is performed.

[0073]

Although a singular reaction vessel may be used for the polycondensation reaction process of PBT or two or more reaction vessels may be used for it, two or more desirable reaction vessels are used for it. the gestalt of a reaction vessel -- a vertical mold stirring complete-mixing tub, a vertical mold heat convection type mixing chamber, and a column -- you may be which types, such as a type successive reaction tub, and these can also be combined. Especially the reaction vessel which has stirring equipment is desirable, and types which carry out a high-speed revolution, such as a turbine stator mold high-speed rotating type [besides / which consists of a power unit, bearing, a shaft, and a stirring aerofoil as stirring equipment / the usual type] agitator, a disc mill mold agitator, and a rotor mill mold agitator, can also be used.

[0074]

Especially the gestalt of stirring is not restricted, but can carry out a part of reaction mixture to the exterior of a reactor for piping besides the usual stirring approach which stirs the reaction mixture in a reaction vessel directly from the upper part of a reaction vessel, the lower part, the transverse part, etc., can stir it with a line mixer etc., and can also take the approach of circulating reaction mixture. Especially, it is recommended at least that one of the polycondensation reaction vessels uses the reactor of the horizontal type excellent in the renewal of a front face which has a revolving shaft horizontally, and self-cleaning nature.

[0075]

Moreover, it is usually 1.3 or less kPa usually still more preferably good [under the high vacuum of 0.3 or less kPas] in at least one reaction vessel, in order to suppress coloring and degradation and to control the increment in ends, such as a vinyl group, preferably to carry

[0060]

However, the number of mols of the 1,4-butanediol by which BM is supplied to per unit time amount from the outside at an esterification reaction vessel, and TM show the number of mols of the terephthalic acid supplied to per unit time amount from the outside at an esterification reaction vessel.

[0061]

When the value of above-mentioned BM/TM is smaller than 1.1, lowering and catalyst deactivation of an invert ratio are caused, and when larger than 4.5, it is in the inclination not only thermal efficiency to fall, but for by-products, such as a tetrahydrofuran, to increase, the value of BM/TM -- desirable -- 1.5-4.0 -- further -- desirable -- 2.0-3.8 -- it is 2.5-3.5 especially preferably.

[0062]

An example of the continuous magnetization method which adopted the ester interchange method is as follows. Within an unit or two or more ester exchange reaction tubs, namely, under existence of a titanium catalyst usually, 110-260 degrees C -- desirable -- 140-245 degrees C -- further -- desirable -- the temperature of 180-220 degrees C -- moreover -- usually -- under the pressure of 60-101kPa still more preferably 13 to 120 kPa preferably ter to 133 kPa It is 1 - 3 hours preferably, an ester exchange reaction product is transported to a polycondensation reaction vessel. Usually, within an unit or two or more polycondensation reaction vessels Under existence of a polycondensation reaction catalyst, still more preferably 20 or less kPas 210-280 degrees C continuous usually preferably the temperature of 220-265 degrees C, and 27 or less kPa usually under reduced pressure of 13 or less kPas Under stirring, a polycondensation reaction is usually carried out preferably in 3 - 10 hours for 2 to 12 hours.

[0063]

As for the mole ratio of terephthalic-acid dialkyl and 1,4-butanediol, in the case of an ester interchange method, it is desirable to fill the following formula (III).

[0064]

[Equation 3]

[0065]

However, the number of mols of the 1,4-butanediol by which BM is supplied to per unit time amount from the outside at an ester exchange reaction tub, and DM show the number of mols of the terephthalic-acid dialkyl supplied to per unit time amount from the outside at an ester exchange reaction tub.

[0066]

When the value of above-mentioned BM/DM is smaller than 1.1, decline in an invert ratio and lowering of catalytic activity are caused, and when larger than 2.5, it is in the inclination not only thermal efficiency to fall, but for by-products, such as a tetrahydrofuran, to increase, the value of BM/DM -- desirable -- 1.1-1.8 -- it is 1.2-1.5 still more preferably.

[0067]

It is total of the 1,4-butanediol which enters in a reaction vessel from the reaction-vessel exterior, such as 1,4-butanediol supplied independently of [the above-mentioned "1,4-butanediol supplied to an esterification reaction vessel from the outside"] these besides the

[0.5 or less-kPa / 225-255-degree C / 230-250-degree C] out at the temperature of 233-245 degrees C still more preferably.

[0076]

Furthermore, after molecular weight is comparatively small, for example, the polycondensation reaction process of PBT manufactures PBT of intrinsic viscosity 0.1 = 0.75 dL/g extent by melt polycondensation, the solid phase polycondensation (solid state polymerization) of it can once be successively carried out at the temperature below the melting point of PBT.

[0077]

Although PBT of this invention does not need to remove the foreign matter concerned since the foreign matter of the catalyst origin is reduced by leaps and bounds, the polymer which was further excellent in quality is obtained by installing a filter in the passage of a polymer precursor or a polymer. In the invention, when the filter of the same opening as what is used by the above-mentioned reason by the manufacturing facility of the conventional PBT is used, it is possible to lengthen the life to the exchange. Moreover, if the life to exchange is similarly set up, it will become possible to install a filter with a still smaller opening.

[0078]

The foreign matter with which the installation location of a filter occurs in the downstream also at remainder of a manufacture process in the case of the upstream is unremovable, and in order to enlarge the opening of a filter in order for the pressure loss of a filter to become large and to maintain a flow rate, or to make a facility of the filtration area of a filter, piping, etc. excessive and to receive high shearing at the time of fluid passage, degradation of PBT: by shear heating becomes unescapable in the place where the viscosity of the downstream is high; therefore, the installation location of a filter -- the intrinsic viscosity of PBT or its precursor -- usually -- the location of 0.5 - 0.8 dL/g is chosen still more preferably 0.2 to 0.8 dL/g preferably 0.1 to 0.8 dL/g.

[0079]

As a filtering medium which constitutes a filter, although any, such as a metal wire, a laminated metal mesh, a metal nonwoven fabric, and a porosity metal plate, are sufficient, that to which a laminated metal mesh or a metal nonwoven fabric is desirable, and the opening is being especially fixed by sintering processing from a viewpoint of a filtration accuracy is desirable. As a configuration of a filter, you may be which types, such as a basket type, a disk type, a leaf disk type, a tube type, a flat mold cylinder type, and a pleat mold cylinder type. Moreover, in order to make it not affect operation of a plant, it is desirable to use it, installing two or more filters and changing, or to install an auto screen changer etc.

[0080]

Although especially the absolute filtration accuracy of a filter is not restricted, it is usually 10-30 micrometers especially preferably 5-50 micrometers still more preferably 2-100 micrometers preferably 0.5-200 micrometers. When a filtration accuracy is too large absolutely, the foreign matter reduction effectiveness in a product is lost, and when too small, lowering of productivity and buildup of filter exchange frequency are caused.

[0081]

Hereafter, the desirable embodiment of the manufacture approach of PBT is explained based on an accompanying drawing. The explanatory view of an example of the polycondensation process which adopts the explanatory view of other examples of the esterification reaction process which adopts the explanatory view, drawing 2, and drawing 3 of an example of the esterification reaction process which adopts drawing 1 by this invention, or an ester exchange reaction process by this invention, and drawing 5-7 are the explanatory views of other examples of the polycondensation process adopted by this invention.

[0082]

In drawing 1, it is mixed with 1,4-butanediol by the raw material mixing chamber (not shown), and the terephthalic acid of a raw material is usually supplied to a reaction vessel (A) with the gestalt of a slurry from a feeding line (1). In the case of terephthalic-acid dialkyl ester, a reaction vessel (A) is usually supplied, without being mixed with 1,4-butanediol. On the other hand, after

there is a possibility that melting kneading with PBT and shaping of a PBT constituent may become difficult.

[0110]

As for a glass fiber, it is desirable that it is the glass fiber from which processing by the finishing agent was made. By processing the front face of a glass fiber by the finishing agent, adhesion or association firm to an interface with PBT and a glass fiber arises, stress is transmitted to a glass fiber from PBT, and the reinforcement effectiveness by the glass fiber is discovered.

[0111]

As a finishing agent to be used, epoxy silane system compounds, such as alkoxysilane system compounds, such as chlorosilane system compounds, such as vinyl trichlorosilane and methylvinyl dichlorosilane, vinyltrimetoxysilane, vinyltriethoxysilane, vinyltriacetoxysilane, and gamma-methacryloxypropyl trimethoxysilane, beta-(3,4-epoxycyclohexyl) ethyltrimethoxysilane, and gamma-glycidylmethacryloxypropyl trimethoxysilane, an acrylic compound, an isocyanate system compound, a titanate compound, epoxy compound, etc. are mentioned, for example.

[0112]

Moreover, as for a glass fiber, it is desirable that it is the glass fiber from which processing by the convergence agent was made. By processing a glass fiber by the convergence agent, the handling workability of a glass fiber can be raised and breakage on a glass fiber can be prevented. As a convergence agent to be used, resin emulsions, such as vinyl acetate resin, an ethylene-vinylacetate copolymer, acrylic resin, an epoxy resin, polyurethane resin, and polyester resin, etc. are mentioned, for example.

[0113]

the hydrolysis-proof nature PBT constituent of this invention -- setting -- the content of an epoxy compound (B) -- the PBT100 weight section -- receiving -- 0.01 - 20 weight section -- it is 0.03 - 10 weight section preferably. When the content of an epoxy compound (B) is under the 0.01 weight section, there is almost no hydrolysis-proof disposition top effectiveness, when exceeding 20 weight sections, other mechanical physical properties fall or heat-of-fusion stability gets worse.

[0114]

moreover, the hydrolysis-proof nature PBT constituent of this invention -- setting -- the content of a consolidation filler (C) -- the PBT100 weight section -- receiving -- the 0 - 200 weight section -- it is the 0 - 150 weight section preferably. When the content of a consolidation filler (C) exceeds the 200 weight sections, there is a possibility that melting kneading and shaping of a resin constituent may become difficult.

[0115]

(Shock-proof PBT constituent)

this invention -- shock resistance -- PBT -- a constituent -- the above -- PBT -- (A) -- 100 -- weight -- the section -- receiving -- an epoxy compound -- (B) -- 0.01 - 20 -- weight -- the section -- a shock resistant -- amelioration -- material -- (D) -- 0.5 - 40 -- weight -- the section -- and -- a consolidation -- a bulking agent -- (C) -- zero - 200 -- weight -- the section -- containing -- things -- the description -- carrying out.

[0116]

The shock-resistant amelioration agent (D) used by this invention raises impact resistance values, such as Izod impact value, Charpy impact value, and a field impact resistance value, and acrylic rubber, butadiene system rubber, silicone system rubber, etc. are mentioned. Especially acrylic rubber is desirable. Acrylic rubber is a rubber-like elasticity object acquired by copolymerization which makes the polymerization of acrylic ester, or it a subject, and the polymer of the shape of rubber which this polymer which was made to carry out the polymerization of acrylic ester like butyl acrylate and a cross-linking monomer like a small amount of butylene diacrylate, and obtained them was made to carry out the graft polymerization of a graft polymerization nature monomer like methyl methacrylate, and obtained it to it as a typical thing is mentioned.

[0117]

As the above-mentioned acrylic ester, methyl acrylate, ethyl acrylate, propylacrylate, hexyl

acrylate, 2-ethylhexyl acrylate, etc. are mentioned other than butyl acrylate. Moreover, as a cross-linking monomer, an allyl compound like a vinyl compound like the ester of polyol, an acrylic acid, or a methacrylic acid like butylene dimethacrylate and trimethylolpropanemethacrylate, a divinylbenzene, vinyl acrylate, and vinyl methacrylate, allyl compound acrylate, allyl compound methacrylate, diallyl maleate, diallyl fumarate, diaryl itaconate, monoallyl malate, monoallyl fumarate, and thoria RIRUSHI nurate etc. is mentioned other than butylene diacrylate.

[0118]

Moreover, as the above-mentioned graft polymerization nature monomer, methacrylic ester like ethyl methacrylate, butyl methacrylate, hexyl methacrylate, 2-ethylhexyl methacrylate, and lauryl methacrylate, styrene, acrylonitrile, etc. are mentioned other than methyl methacrylate. In case the polymerization of the above-mentioned acrylic ester and the cross-linking monomer is carried out for that part and a polymer is manufactured, copolymerization of this graft polymerization nature monomer can be used and carried out.

[0119]

the shock-proof PBT constituent of this invention -- setting -- the content of a shock-resistant amelioration agent (D) -- the PBT100 weight section -- receiving -- 0.5 - 40 weight section -- desirable -- 1 - 35 weight section -- it is 2 - 30 weight section still more preferably. When improvement in shock resistance or heat shock-proof nature is not accepted when the content of a shock-resistant amelioration agent (D) is under the 0.5 weight section, but exceeding 40 weight sections, lowering of mechanical properties, such as tensile strength and flexural strength, is remarkable.

[0120]

Let the class and content of an epoxy compound (B) and a consolidation filler (C) be a class and a content same with having explained in the above-mentioned hydrolysis-proof nature PBT constituent in the shock-proof PBT constituent of this invention.

[0121]

(Fire-resistant PBT constituent)
this invention -- fire retardancy -- PBT -- a constituent -- the above -- PBT -- (A) -- 100 -- weight -- the section -- receiving -- bromination -- an aromatic compound -- a system -- a flame retarder -- (E) -- three - 50 -- weight -- the section -- an antimony compound -- (F) -- one - 30 -- weight -- the section -- dropping -- an inhibitor -- (G) -- zero - 15 -- weight -- the section -- and -- a consolidation -- a filler -- (C) -- zero - 200 -- weight -- the section -- containing -- things -- the description -- carrying out.

[0122]

It is the aromatic series system compound known as a bromine system flame retarder used for resin as a bromination aromatic compound system flame retarder (E) used by this invention, for example, the epoxy oligomer of tetrabromobisphenol A, Pori (pen TABUROMO benzyl acrylate), poly BUROMO phenyl ether, bromine-ized polystyrene, bromine-ized epoxy, bromine-ized imide, a bromine-ized polycarbonate, etc. are mentioned.

[0123]

As an antimony compound (F) used by this invention, antimony oxide and an antimonate are mentioned and antimonates, such as oxide, such as an antimony trioxide (Sb 2O3), antimony tetroxide (Sb 2O4), and antimony pentoxide (Sb 2O5), or sodium antimonate, are mentioned as an example, for example.

[0124]

The dropping inhibitor (G) used by this invention points out the compound which has the property to prevent dropping of the resin at the time of combustion, and sheet silicates, such as a mica besides a silicone oil, a silica, asbestos, a fluororesin, and talc, etc. are mentioned as the concrete example. Especially a dropping inhibitor desirable from a fire-resistant viewpoint of a constituent is a fluorine content polymer or a sheet silicate.

[0125]

As an example of the fluororesin used as a dropping inhibitor (G), fluorination polyolefines, such as polytetrafluoroethylene, tetrafluoroethylene / perfluoroalkyl vinyl ether copolymer.

http://www4.ipdl.ncipi.go.jp/cgi-bin/tran_web.cgi.eje

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tetrafluoroethylene / hexafluoropropylene copolymer, tetrafluoroethylene / ethylene copolymer; vinylidene fluoride, and polychlorotrifluoroethylene resin, etc. are mentioned. In these, polytetrafluoroethylene, tetrafluoroethylene / perfluoroalkyl vinyl ether copolymer, tetrafluoroethylene / hexafluoropropylene copolymer, and tetrafluoroethylene / ethylene copolymer are desirable, and polytetrafluoroethylene, tetrafluoroethylene / hexafluoropropylene copolymer is still more desirable.

[0126]

As polytetrafluoroethylene, what has fibril organization potency is desirable. That is, it distributes easily in resin, and the inclination which polymers join together and makes a fibrous ingredient is shown, and it functions as a dropping inhibitor. The polytetrafluoroethylene which has fibril organization potency is classified into Type 3 according to ASTM specification, for example, can come to hand commercially as "Fluon CD-123" of "Pori Flon FA-500" or "F-201L" of Daikin Chemical industry, and Asahi Glass Co., Ltd., and "(Teflon R) 6J" of Dupont-Mitsui Fluorochemicals, Inc.

[0127]

the melt viscosity in 350 degrees C of the fluororesin used as a dropping inhibitor (G) -- usually -- 1.0x10² to 1.0x10³ (Pa·s) -- desirable -- 1.0x10³ to 1.0x10⁴ (Pa·s) -- it is 1.0x10¹⁰ to 1.0x10¹² (Pa·s) still more preferably. When melt viscosity is under 1.0x10² (Pa·s), the dropping prevention ability at the time of combustion is inadequate, and when larger than 1.0x10¹⁵ (Pa·s), the fluidity of a constituent falls remarkably.

[0128]

It is desirable from a fluid viewpoint at the time of melting of the resin constituent of this invention to use a sheet silicate as a dropping inhibitor (G). Although a sheet silicate, a denaturation sheet silicate (sheet silicate which inserted the 4th class organic onium cation between layers), the sheet silicate that gave the reactant functional group, or a denaturation sheet silicate is mentioned as a sheet silicate from the dispersibility to this invention resin constituent of a sheet silicate, and a viewpoint of dropping prevention ability A' denaturation sheet silicate, the sheet silicate which added the reactant functional group, or a denaturation sheet silicate is desirable, and the sheet silicate or denaturation sheet silicate which added reactant functional groups, such as an epoxy group, an amino group, an oxazoline radical, a carboxyl group, and an acid anhydride, especially is used suitably. As the functional-group grant approach, the approach of processing with an organic-functions-sized reagent (silane coupling agent) is easy, and desirable.

[0129]

As an organic-functions-sized reagent, the chlorosilanes in which a metaphor has an epoxy group, the chlorosilanes which have a carboxyl group, the chlorosilanes which have a sulphydryl group, the alkoxy silane which have an amino group, and the alkoxy silane which have an epoxy group are mentioned. Especially 3-glycidylmethacryloxy propyl dimethylchlorosilane, beta-(3,4-epoxycyclohexyl) ethyl dimethylchlorosilane, The chlorosilanes which have epoxy groups, such as 3-glycidylmethacryloxy propyl trimethylsilane 3-amino propyl triethoxysilane, N-(2-aminoethyl)-3-aminopropyl trimethoxysilane, The alkoxy silane which has amino groups, such as N-(2-aminoethyl)-3-aminopropyl methyl dimethoxysilane The alkoxy silane which has epoxy groups, such as 3-glycidylmethacryloxy propyl diethoxysilane, 3-glycidylmethacryloxy propyl trimethoxysilane, and gamma-(3,4-epoxycyclohexyl) ethyltrimethoxysilane, is desirable. It is desirable that mixing in a non-solvent or a polar solvent performs contact to the sheet silicate of these organic-functions-sized reagent.

[0130]

As an example of the sheet silicate used by this invention, bloating tendency synthetic mica, such as smectite system clay minerals, such as a montmorillonite, hectorite, fluorine hectorite, saponite, beidellite, and a SUBUCHIN site, Li mold fluorine TENIO light, Na mold fluorine TENIO light, a Na mold 4 silicon fluorine mica, and a Li mold 4 silicon fluorine mica, a vermiculite, a fluorine vermiculite, halloysite, etc. may be mentioned, and any of a natural article and synthetic compounds are sufficient. Especially, bloating tendency synthetic mica, such as smectite system clay minerals, such as a montmorillonite and hectorite, Li mold fluorine TENIO light, Na mold

fluorine TENIO light, and a Na mold 4 silicon fluorine mica, is desirable.

[0131]

As the 4th class onium cation inserted between the layers of the denaturation sheet silicate used by this invention For example, trimethyl octyl ammonium, trimethyl DESHIRU ammonium, Trimethyl dodecyl ammonium, trimethyl tetradecyl ammonium, Trimethyl alkyl ammonium, such as trimethyl hexadecyl ammonium and trimethyl octadecyl ammonium, Dimethyl dioctyl ammonium, dimethyl JIDESHIRU ammonium, Dimethyl dialkyl ammonium, such as dimethyl dodecyl ammonium; dimethyl JITETORA ammonium, JIMECHIRUJI hexadecyl ammonium, and dimethyl dioctadecyl ammonium, etc. is mentioned.

[0132]

As a dropping inhibitor (G), a silicone oil is also desirable. It is the compound which has the dimethylpolysiloxane frame expressed with the following general formula (1) as a silicone oil, and some or all of an end or a side chain receives amino denaturation, epoxy denaturation, carboxyl denaturation, carbonil denaturation, methacrylic denaturation, mercapto denaturation, phenol denaturation, polyether denaturation, methyl styrol denaturation, alkyl denaturation, higher-fatty-acid ester denaturation, high-class alkoxy denaturation, and fluorine denaturation, and may be functionalized.

[0133]

[Formula: 1]
$$\left(\text{CH}_3\text{Si}(\text{R})_2\text{O} \right)_n$$

the viscosity of the silicone oil used as a dropping inhibitor (G) -- 25 degrees C -- setting -- usually -- 1000-30000 (cs) -- desirable -- 2000-25000 (cs) -- it is 3000-20000 (cs) still more preferably. When viscosity is under 1000 (cs), the dropping prevention operation under combustion becomes less enough, fire retardancy falls greatly, and when larger than 30000 (cs), the fluidity of a constituent falls remarkably according to the thickening effectiveness.

[0134]

the viscosity of the silicone oil used as a dropping inhibitor (G) -- 25 degrees C -- setting -- usually -- 1000-30000 (cs) -- desirable -- 2000-25000 (cs) -- it is 3000-20000 (cs) still more preferably. When viscosity is under 1000 (cs), the dropping prevention operation under combustion becomes less enough, fire retardancy falls greatly, and when larger than 30000 (cs), the fluidity of a constituent falls remarkably according to the thickening effectiveness.

[0135]

the fire-resistant PBT constituent of this invention -- setting -- the content of a bromination aromatic compound system flame retarder (E) -- the PBT100 weight section -- receiving -- 3 - 50 weight section -- desirable -- 5 - 40 weight section -- it is 8 - 30 weight section still more preferably. When the content of a bromination aromatic compound system flame retarder (E) is under 3 weight sections, fire-resistant effectiveness is inadequate, when exceeding 50 weight sections, a mechanical strength falls and the thermal stability at the time of melting tends to fall.

[0136]

the fire-resistant PBT constituent of this invention -- setting -- the content of an antimony compound (F) -- the PBT100 weight section -- receiving -- 1 - 30 weight section -- desirable -- 2 - 25 weight section -- it is 3 - 20 weight section still more preferably. When sufficient fire-resistant effectiveness is not acquired when the content of an antimony compound (F) is under 1 weight section, but exceeding 30 weight sections, a mechanical strength falls and the thermal stability at the time of melting tends to fall.

[0137]

In the fire-resistant PBT constituent of this invention, the content of a dropping inhibitor (G) is 0 - 15 weight section to the PBT100 weight section. When the content of a dropping inhibitor (G) exceeds 15 weight sections, there is a possibility of causing lowering of a fluidity or mechanical

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tetrafluoroethylene / hexafluoropropylene copolymer, tetrafluoroethylene / ethylene copolymer; vinylidene fluoride, and polychlorotrifluoroethylene resin, etc. are mentioned. In these,

polytetrafluoroethylene, tetrafluoroethylene / perfluoroalkyl vinyl ether copolymer,

tetrafluoroethylene / hexafluoropropylene copolymer, and tetrafluoroethylene / ethylene copolymer are desirable, and polytetrafluoroethylene, tetrafluoroethylene / hexafluoropropylene copolymer is still more desirable.

[0126]

As polytetrafluoroethylene, what has fibril organization potency is desirable. That is, it distributes easily in resin, and the inclination which polymers join together and makes a fibrous ingredient is shown, and it functions as a dropping inhibitor. The polytetrafluoroethylene which has fibril organization potency is classified into Type 3 according to ASTM specification, for example, can come to hand commercially as "Fluon CD-123" of "Pori Flon FA-500" or "F-201L" of Daikin Chemical industry, and Asahi Glass Co., Ltd., and "(Teflon R) 6J" of Dupont-Mitsui Fluorochemicals, Inc.

[0127]

the melt viscosity in 350 degrees C of the fluororesin used as a dropping inhibitor (G) -- usually -- 1.0x10² to 1.0x10³ (Pa·s) -- desirable -- 1.0x10³ to 1.0x10⁴ (Pa·s) -- it is 1.0x10¹⁰ to 1.0x10¹² (Pa·s) still more preferably. When melt viscosity is under 1.0x10² (Pa·s), the dropping prevention ability at the time of combustion is inadequate, and when larger than 1.0x10¹⁵ (Pa·s), the fluidity of a constituent falls remarkably.

[0128]

It is desirable from a fluid viewpoint at the time of melting of the resin constituent of this invention to use a sheet silicate as a dropping inhibitor (G). Although a sheet silicate, a denaturation sheet silicate (sheet silicate which inserted the 4th class organic onium cation between layers), the sheet silicate that gave the reactant functional group, or a denaturation sheet silicate is mentioned as a sheet silicate from the dispersibility to this invention resin constituent of a sheet silicate, and a viewpoint of dropping prevention ability A' denaturation sheet silicate, the sheet silicate which added the reactant functional group, or a denaturation sheet silicate is desirable, and the sheet silicate or denaturation sheet silicate which added reactant functional groups, such as an epoxy group, an amino group, an oxazoline radical, a carboxyl group, and an acid anhydride, especially is used suitably. As the functional-group grant approach, the approach of processing with an organic-functions-sized reagent (silane coupling agent) is easy, and desirable.

[0129]

As an organic-functions-sized reagent, the chlorosilanes in which a metaphor has an epoxy group, the chlorosilanes which have a carboxyl group, the chlorosilanes which have a sulphydryl group, the alkoxy silane which have an amino group, and the alkoxy silane which have an epoxy group are mentioned. Especially 3-glycidylmethacryloxy propyl dimethylchlorosilane, beta-(3,4-epoxycyclohexyl) ethyl dimethylchlorosilane, The chlorosilanes which have epoxy groups, such as 3-glycidylmethacryloxy propyl trimethylsilane 3-amino propyl triethoxysilane, N-(2-aminoethyl)-3-aminopropyl trimethoxysilane, The alkoxy silane which has amino groups, such as N-(2-aminoethyl)-3-aminopropyl methyl dimethoxysilane The alkoxy silane which has epoxy groups, such as 3-glycidylmethacryloxy propyl diethoxysilane, 3-glycidylmethacryloxy propyl trimethoxysilane, and gamma-(3,4-epoxycyclohexyl) ethyltrimethoxysilane, is desirable. It is desirable that mixing in a non-solvent or a polar solvent performs contact to the sheet silicate of these organic-functions-sized reagent.

[0130]

As an example of the sheet silicate used by this invention, bloating tendency synthetic mica, such as smectite system clay minerals, such as a montmorillonite, hectorite, fluorine hectorite, saponite, beidellite, and a SUBUCHIN site, Li mold fluorine TENIO light, Na mold fluorine TENIO light, a Na mold 4 silicon fluorine mica, and a Li mold 4 silicon fluorine mica, a vermiculite, a fluorine vermiculite, halloysite, etc. may be mentioned, and any of a natural article and synthetic compounds are sufficient. Especially, bloating tendency synthetic mica, such as smectite system clay minerals, such as a montmorillonite and hectorite, Li mold fluorine TENIO light, Na mold

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physical properties.

[0138]

Let the class and content of a consolidation filler (O) be a class and a content same with having explained in the above-mentioned hydrolysis-proof nature PBT constituent in the fire-resistant PBT constituent of this invention.

[0139]

(Non-halogen fire retardancy PBT constituent)

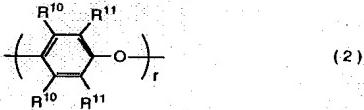
this invention -- fire retardancy -- PBT -- a constituent -- the above -- PBT -- (A) -- 50 -- 95 -- weight -- the section -- polyphenylene ether -- resin -- (H) -- five -- 50 -- weight -- the section -- a total -- 100 -- weight -- the section -- receiving -- at least one sort of (Compound J) 2--45 chosen from a compatibilizer (I) 0.05 -- 10 weight sections, phosphoric ester, or phospho nitril -- weight -- the section -- a consolidation -- a filler -- (C) -- zero -- 200 -- weight -- the section -- dropping -- an inhibitor -- (G) -- zero -- 15 -- weight -- the section -- cyanuric acid -- a melamine -- (K) -- zero -- 45 -- weight -- the section -- and -- boric acid -- a metal -- a salt -- (L) -- zero -- 50 -- weight -- the section -- containing -- things -- the description -- carrying out.

[0140]

It is the homopolymer or copolymer which has the structure shown by the following general formula (2) (is written as Following PPE). [the polyphenylene ether resin (H) used by this invention, and]

[0141]

[Formula 2]



[0142]

(R10 expresses a hydrogen atom, the first class or the second class alkyl group, an aryl group, an amino alkyl group, or a hydrocarbon oxy-radical among a formula, and R11 expresses the first class or the alkyl group of the second class, an aryl group, or an alkylamino radical, r expresses ten or more integers.)

[0143]

As a first-class alkyl group shown by R10, a methyl group, an ethyl group, n-propyl group, n-butyl, n-amyl group, n-hexyl group, an isoamyl radical, 2-methylbutyl radical, 2, 3-dimethylbutyl, 2-, 3-, 4-methyl pentyl radical, or a heptyl radical is mentioned, for example. As a suitable example of the second class alkyl group, an isopropyl group, sec-butyl, or 1-ethyl propyl group is mentioned. As a suitable homopolymer of PPE, it consists of 2, the 6-dimethyl-1, and 4-phenylene ether unit; for example. As a suitable copolymer, it is the above-mentioned unit and 2, 3, and 6-trimethyl. It is the random copolymer which consists of combination of 1 and 4-phenylene ether unit.

[0144]

the intrinsic viscosity in 30 degrees C measured in the chloroform of PPE (H) used by this invention -- usually -- it is 0.3 -- 0.8 dL/g still more preferably 0.25 to 0.7 dL/g preferably 0.2 to 0.8 dL/g. When the shock resistance of a constituent becomes inadequate when intrinsic viscosity is less than 0.2 dL/g, and exceeding 0.8 dL/g, there are many gel components and there is an inclination for a mold-goods appearance to get worse.

[0145]

which may contain the oxygen atom, the nitrogen atom, or the sulfur atom.) R16 shows the permutation or unsubstituted arylene radical of the alkylene group of carbon numbers 1-20, or carbon numbers 6-30, when u is 1, and when u is 2, it shows the alkyltetrayl group of carbon numbers 4-18.

[0153]

As an example of R15, a methyl group, an ethyl group, a propyl group, an octyl radical, An iso octyl radical, an isodecyl radical, a decyl group, a stearyl radical, a lauryl radical, Phenyl group, 2-, 3-, or 4-methylphenyl radical, 2, and 4- or 2, 6-dimethylphenyl radical, 2, 3, 6-trimethyl phenyl radical, 2-, 3-, or 4-ethyl phenyl group, 2-, 4- or 2-, 6-dimethyl phenyl group, 2 and 3, 6-triethyl phenyl group, 2-, 3- or 4-tert-butylphenyl radical, 2, and 4- or 2, 6-G tert-butylphenyl radical, 2, a 6-G tert-butyl-4-methylphenyl radical, 2, a 6-G tert-butyl-4-ethyl phenyl group, An octyl phenyl group; an iso octyl phenyl group, 2-, 3- or 4-nonylphenyl radical, 2, 4-dimethoxy phenyl radical, a biphenyl radical, a naphthyl group, etc. are mentioned. Especially, a permutation or unsubstituted aryl groups are desirable.

[0154]

As R16, it is a general formula (4) and polymethylene radicals, such as 1, 2-phenylene group, ethylene, a propylene, trimethylene, tetramethylene, and hexamethylene, are mentioned at the time of u=1.

[0155]

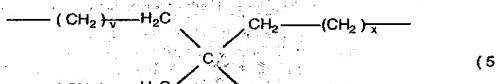
Phosphite when u is 1 as an example of the compound of a general formula (4) (phenyl) (1,3-propanediol), Phosphite, (4-methylphenyl) (1,3-propanediol) Phosphite, (2, 6-dimethylphenyl) (1,3-propanediol) Phosphite, (4-tert-butylphenyl) (1,3-propanediol) Phosphite, (2, 6-G tert-butylphenyl) (1,3-propanediol) Phosphite, (2, 6-G tert-butyl-4-methylphenyl) (1,3-propanediol) Phosphite, (2, 6-G tert-butyl-4-ethylphenyl) (1,3-propanediol) Phosphite, (1,2-ethanediol) (4-methylphenyl) (Phenyl) (1,2-ethanediol) Phosphite, (2, 6-dimethylphenyl) (1,2-ethanediol) Phosphite, (4-tert-butylphenyl) (1,2-ethanediol) Phosphite, (2, 6-G tert-butylphenyl) (1,2-ethanediol) (2, 6-G tert-butyl-4-methylphenyl) Phosphite, phosphite (1,4-butenediol) (2, 6-G tert-butyl-4-methylphenyl), etc. are mentioned (1,2-ethanediol).

[0156]

Moreover, the tetrayl radical of the pentaerythritol structure which shows R16 in the following general formula (5) etc. is mentioned at the time of u=2.

[0157]

[Formula 5]



(式中、v、w、x、yはそれぞれ0~6の整数を示す。)

[0158]

As an example, diisodecyl pentaerythritoldiphosphite, Diisauryl pentaerythritoldiphosphite, distearyl pentaerythritoldiphosphite, Diphenyl pentaerythritoldiphosphite, bis(2-methylphenyl) pentaerythritoldiphosphite, Bis(3-methylphenyl) pentaerythritoldiphosphite, Bis(4-methylphenyl) pentaerythritoldiphosphite, Bis(2, 4-dimethylphenyl) pentaerythritoldiphosphite, Bis(2, 6-trimethyl phenyl) BENTA erythritol diphosphite, Bis(2-tert-butylphenyl) pentaerythritoldiphosphite, Bis(3-tert-butylphenyl) pentaerythritoldiphosphite, Bis(4-tert-butylphenyl) pentaerythritoldiphosphite, Bis(2, 4-G tert-

The compatibilizer (I) used by this invention is a compound which raises the dispersibility of PPE in PBT, and a compound, a phosphite compound, etc. which have polycarbonate resin, a carboxyl group, a carboxylic acid, an acid-anhydride radical, an imide radical, an acid-anhydride radical, an epoxy group, an oxazolinyl radical, an amino group, and one or more functional groups chosen from the group of a hydroxyl group can be used.

[0146]

As an example of a compound of having a functional group, epoxy group addition PPE resin, hydroxylalkyl-ized PPE resin, end oxazoline-ized PPE resin, the polyester, in which the carboxyl group end denaturalized by polystyrene, the polyester in which the OH radical end denaturalized with polyethylene are mentioned.

[0147]

The phosphorous acid triester to which phosphorous acid triester is desirable and is especially expressed [in / phosphite or polycarbonate resin is desirable / phosphite] with the following general formula (3) or (4) as a compatibilizer (I) from the hydrolysis-proof nature of this invention constituent, crystallinity, mechanical physical properties, and a fire-resistant viewpoint is desirable.

[0148]

[Formula 3]



[0149]

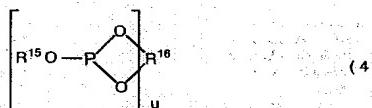
(R12-R14 show respectively the permutation or unsubstituted aryl group of the alkyl group of carbon numbers 1-20 or carbon numbers 6-30 which may contain the oxygen atom, the nitrogen atom, and the sulfur atom independently among a formula.)

[0150]

As an example of a general formula (3), trioctyl phosphite, tridecyl phosphite, Trilauryl phosphite, tristearylphosphite, tri-iso-octyl phosphite, Tris(nonylphenyl) phosphite, tris (2, 4-dinonylphenyl) phosphite, Tris (2, 4-G tert-butylphenyl) phosphite, triphenyl phosphite, Tris (octyl phenyl) phosphite, diphenyl isooctylphosphite, Diphenyl isodecyl phosphite, octyl diphenyl phosphite, diisauryl phenyl phosphite, diisodecyl phenyl phosphite, bis(nonylphenyl) phenyl phosphite, JISOC octyl phenyl phosphite, etc. are mentioned.

[0151]

[Formula 4]



(u is 1 or 2 among a formula, or R15 is the same, it differs and it shows the permutation or unsubstituted aryl group of the alkyl group of carbon numbers 1-20 or carbon numbers 6-30

buthylphenyl) pentaerythritoldiphosphite, Bis(2, 6-G tert-butylphenyl) pentaerythritoldiphosphite, Bis(2, 6-G tert-butyl-4-methylphenyl) pentaerythritoldiphosphite, Bis(2, 6-G tert-butyl-4-ethyl phenyl) pentaerythritoldiphosphite, Bis(nonylphenyl) pentaerythritoldiphosphite, bis(biphenyl) pentaerythritoldiphosphite, dinaphthyl pentaerythritoldiphosphite, etc. are mentioned.

[0159]

In the above-mentioned phosphorous acid triester, in a formula (4), the compound in which u is shown by 1 or 2 is desirable, and the compound whose R16 are the tetrayl radical of the pentaerythritol structure shown in a general formula (5) etc. in u=2 of a formula (4) is more more desirable still. Also in it, bis(nonylphenyl)pentaerythritoldiphosphite, bis(2, 4-G tert-butylphenyl) pentaerythritoldiphosphite, bis(2, 6-G tert-butyl-4-methylphenyl) pentaerythritoldiphosphite, etc. are more desirable, and bis(2, 4-G tert-butylphenyl) pentaerythritoldiphosphite and bis(2, 6-G tert-butyl-4-methylphenyl) pentaerythritoldiphosphite are especially desirable. In addition, the constituent of this invention may contain the compound produced by decomposition (hydrolysis, pyrolysis, etc.) of these phosphorous acid triester.

[0160]

The thermoplastic aromatic series polycarbonate polymer or copolymer which is manufactured by making an aromatic series dihydroxy compound, or this and a little polyhydroxy compound react with the diester of a phosgene or carbonic acid as polycarbonate resin used as a compatibilizer (I) in this invention and which may branch is mentioned.

[0161]

As an aromatic series dihydroxy compound, 2 and 2-bis(4-hydroxyphenyl) propane (= bisphenol A), tetramethyl biphenol A, bis(4-hydroxyphenyl)-p-disopropylbenzene, hydroquinone, resorcinol, 4, and 4-dihydroxydiphenyl etc. is mentioned, and it is bisphenol A preferably.

[0162]

In order to obtain branched polycarbonate resin, it is phloroglucine, 4, and 6-dimethyl-2, 4-Tori (4-hydroxyphenyl) heptene - 2, 4, 6-dimethyl - 2, 4, 6-Tori (4-hydroxyphenyl) heptane, 2, 6-dimethyl - 2, 4, 6-Tori (4-hydroxyphenyl) heptene - 3, 1, 3, 5-tris (4-hydroxyphenyl) benzene. The polyhydroxy compound shown by 1, 1, and 1-tris (4-hydroxyphenyl) ethane etc., Or a 3 and 3-bis(4-hydroxy aryl) oxy-indole (= isatin bisphenol), 5-KURORU isatin, 5, a 7-dichloro isatin, 5-bromine isatin, etc. -- as said some of aromatic series dihydroxy compounds -- using it --- ***ing -- the amount used -- usually, -- 0.01-10-mol % -- it is 0.1-2-mol % preferably.

[0163]

As aromatic series polycarbonate resin, the polycarbonate copolymer guided from a polycarbonate resin [which is guided from a 2 and 2-bis(4-hydroxyphenyl) propane] or 2, and 2-bis(4-hydroxyphenyl) propane and other aromatic series dihydroxy compounds is mentioned preferably.

[0164]

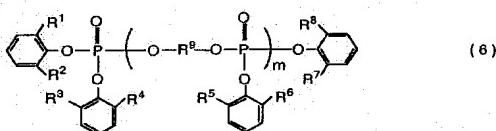
as the viscosity average molecular weight converted from the solution viscosity which the methylene chloride was used for the molecular weight of the polycarbonate resin used as a compatibilizer (I) as a solvent, and was measured at the temperature of 25 degrees C -- usually -- 16,000-30,000 -- it is 18,000-23,000 preferably. As polycarbonate resin, two or more sorts of polycarbonate resin can also be mixed and used.

[0165]

Wide range phosphoric ester is included as a phosphoric ester compound (J) used by this invention. As the example, although trimethyl phosphate, triethyl phosphate, tributyl phosphate, triethylphosphate, tributoxyethyl phosphate, triphenyl phosphate, tricresyl phosphate, cresyl diphenyl phosphate, octyl diphenyl phosphate, etc. are mentioned, the compound especially expressed with the following general formula (6) is desirable.

[0166]

[Formula 6]



[0167]

(R1-R8) show a hydrogen atom or the alkyl group of carbon numbers 1-6 independently among a formula, respectively, and m is the integer of 0, or 1-4.) R9 is a divalent radical chosen from a p-phenylene group, m-phenylene group, 4, and 4'-biphenylene radical or the following.

[0168]

[Formula 7]



[0169]

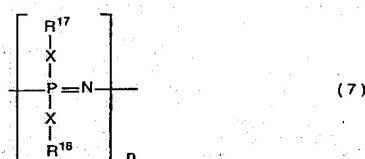
from a viewpoint which raises the hydrolysis-proof nature of this invention constituent in the aforementioned general formula (6) as for R1-R8 — desirable — a with a carbon number of six or less alkyl group — further — desirable — a with a carbon number of two or less alkyl group — it is a methyl group especially preferably. m — desirable — 1-3 — it is 1 still more preferably. R9 — desirable — p-phenylene group or m-phenylene group — it is m-phenylene group still more preferably.

[0170]

Moreover, the phospho nitril compound which has the radical expressed with the following general formula (7) as a component (L) is also used suitably.

[0171]

[Formula 8]



[0172]

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explained in the above-mentioned hydrolysis-proof nature PBT constituent in the non-halogen fire retardancy PBT constituent of this invention.

[0181]

Let the class and content of a dropping inhibitor (G) be a class and a content same with having explained in the above-mentioned fire-resistant PBT constituent in the non-halogen fire retardancy PBT constituent of this invention.

[0182]

the case where a dropping inhibitor (G) is a sheet silicate in the non-halogen fire retardancy PBT constituent of this invention — the content — a total of 100 weight sections of PBT and PPE — receiving — 0-15 weight section — desirable — 0.3-12 weight section — it is 0.5-10 weight section still more preferably. When content of a sheet silicate exceeds 15 weight sections, a fluidity and mechanical physical properties fall extremely. In addition, a sheet silicate may use one kind and may use two or more sorts together.

[0183]

the case where a dropping inhibitor (G) is a silicone oil in the non-halogen fire retardancy PBT constituent of this invention — the content — a total of 100 weight sections of PBT and PPE — receiving — 0-15 weight section — it is — desirable — 0.005-8 weight section — it is 0.005-5 weight section still more preferably. When content of a silicone oil exceeds 15 weight sections, a fluidity and a mechanical property deteriorate remarkably.

[0184]

the non-halogen fire retardancy PBT constituent of this invention — setting — the content of a cyanuric acid melamine (K) — a total of 100 weight sections of PBT and PPE — receiving — 0-45 weight section — desirable — 3-40 weight section — it is 5-30 weight section still more preferably. When the content of a cyanuric acid melamine (K) exceeds 45 weight sections, toughness and ductility are reduced or bleed out and a plate out are caused.

[0185]

the ratio of at least one sort of compounds (U) chosen from phosphoric ester or phospho nitril in the non-halogen fire retardancy PBT constituent of this invention; and a cyanuric acid melamine (K) — usually — 1:9-9:1 — desirable — 2:8-8:2 — it is 2.5:7.5 to 7.5:2.5 still more preferably.

[0186]

the non-halogen fire retardancy PBT constituent of this invention — setting — the content of a boric acid metal salt (L) — a total of 100 weight sections of PBT and PPE — receiving — 0-50 weight section — desirable — 2-45 weight section — it is 3-40 weight section still more preferably. When the content of a boric acid metal salt (L) exceeds 50 weight sections, mechanical physical properties tend to fall.

[0187]

In this invention, the approach of adding an additive by melting kneading is desirable as an approach of making PBT containing various additives. As a melting kneading method, the kneading approach regularly used about thermoplastics is applicable. For example, with the component additionally added by the need, each component is kneaded using a shaft kneading extruder, a multiaxial kneading extruder, a roll, a Banbury mixer, Brabender, etc., after mixing to homogeneity with a Henschel mixer, a ribbon blender, a V type blender, etc.

[0188]

Each component can be collectively supplied to a kneading machine including an additional component, or sequential supply can also be carried out. Moreover, two or more sorts of components, including an additional component chosen from each component are also mixable beforehand. By adding, after resin fuses from the middle of an extruder, consolidation system fillers, such as a glass fiber, can avoid crushing, and can demonstrate a high property. Moreover, when adding a liquefied epoxy compound, and PBT presses an epoxy compound fit from the middle of an extruder to the inside by which melting kneading is carried out, you may add.

[0189]

PBT of this invention and especially the fabricating-operation approach of the constituent are not restricted, but can apply the fabricating methods, such as the fabricating method currently generally used about thermoplastics, i.e., injection molding, blow molding, extrusion molding, and

(X expresses -O-, -S-, -NH-, or direct coupling among a formula.) R17 and R18 show the aryl group of carbon numbers 1-20, an alkyl group, and a cycloalkyl radical. Even if R17-X- and R18-X- are the same, they may differ. n shows the integer of 1-12.

[0173]

In a general formula (7), aryl groups, such as cycloalkyl radicals, such as an alkyl group by which a methyl group, an ethyl group, butyl, a hexyl group, benzyl, etc. may be permuted, and cyclohexyl, a phenyl group, and naphthyl, are mentioned as an example of R17 and R18. n is 3-10 preferably and is 3 or 4 still more preferably. Although the phospho nitril compound of a general formula (7) may be a linear polymer or may be an annular polymer, its annular polymer is desirable. -O- or -NH- of X is desirable and especially its -O- is desirable.

[0174]

As an example of the phospho nitril compound shown by the general formula (7), hexa phenoxy cyclotriphenophosphazene, hexa (hydroxy phenoxy) cyclotriphenophosphazene, OKUTA phenoxy cyclotriphenophosphazene, OKUTA (hydroxy phenoxy) cyclotriphenophosphazene, etc. are mentioned.

[0175]

The cyanuric acid melamine (K) used by this invention is the abbreviation equimolar reactant of cyanuric acid and a melamine, for example, the water solution of cyanuric acid and the water solution of a melamine are mixed, and it can be made to be able to react under stirring at the temperature of 90-100 degrees C, and can obtain by filtering the generated precipitation. 0.01-1000 micrometers of particle size of a cyanuric acid melamine are usually 0.01-500 micrometers preferably. Some of amino groups of a cyanuric acid melamine or hydroxyl groups may be permuted by other substituents.

[0176]

It is stable under the usually used processing conditions, and the boric acid metal salt (L) used by this invention has a desirable thing without a volatile constituent. As a boric acid metal salt (L), the alkali-metal salts (for example, sodium tetraborate, a metaboric acid potassium, etc.) of boracic acid, alkaline earth metal salts (for example, boracic acid calcium, boroboric magnesium, orthoboracic barium, zinc borate, etc.), etc. are mentioned. In these, zinc borate is desirable. Generally zinc borate is shown by Zn₂O, 3B₂-203, and xH₂O (x=3-37). As hydration zinc borate, preferably, it is expressed with the formula of 2ZnO and 3B₂-203.5H₂O, and is stable to temperature higher than 260 degrees C or it.

[0177]

the non-halogen fire retardancy PBT constituent of this invention — setting — the content of polyphenylene ether (H) and (PPE) — as the weight ratio of PBT:PPE — 95.5-50:50 — desirable — 92.8-55:45 — it is 90.10-60:40 still more preferably. When the ratio of PPE is less than five, the fire retardancy of a constituent and hydrolysis-proof nature become inadequate, and when exceeding 50, the fluidity and chemical resistance of a constituent fall remarkably.

[0178]

the non-halogen fire retardancy PBT constituent of this invention — setting — the content of a compatibilizer (I) — a total of 100 weight sections of PBT and PPE — receiving — 0.05-10 weight section — desirable — 0.1-8 weight section — it is 0.3-5 weight section still more preferably. When the content of a compatibilizer (I) is under the 0.05 weight section, the physical properties of a constituent, especially a mechanical strength and fire retardancy fall, and when exceeding 10 weight sections, fire retardancy and the surface appearance of a product fall.

[0179]

the non-halogen fire retardancy PBT constituent of this invention — setting — the content of phosphoric ester or phosphonium (J) — a total of 100 weight sections of PBT and PPE — receiving — 2-45 weight section — desirable — 3-40 weight section — it is 5-30 weight section still more preferably. When the content of phosphoric ester or phosphonium (J) is under 2 weight sections, the fire retardancy of a constituent becomes inadequate, and when exceeding 45 weight sections, hydrolysis-proof [mechanical physical properties and] nature and a moldability fall remarkably.

[0180]

Let the class and content of a consolidation filler (C) be a class and a content same with having

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press forming.

[0190]

Since PBT of this invention is excellent in a color tone, hydrolysis-proof nature, thermal stability, transparency, and a moldability, it is suitable as injection-molding components, such as electrical and electric equipment, electronic parts, and components for automobiles.

[Example]

[0191]

Hereafter, although an example explains this invention to a detail further, this invention is not limited to the following examples at all, unless the summary is exceeded. In addition, the physical properties adopted in many following examples and the measuring method of evaluation criteria are as follows.

[0192]

(1) Rate of esterification: the acid number and saponification value by the following formulas (IV). The acid number dissolved oligomer in dimethylformamide and it asked for it with titration using 0.1-N KOH/methanol solution. Saponification value hydrolyzed oligomer with 0.5-N KOH / ethanol solution, and titrated-and-asked for it with the 0.5-N hydrochloric acid.

[0193]

[Equation 4]
$$\text{エスチル化率} = \left[(\text{ケン化値}-\text{酸値}) / (\text{ケン化値}) \right] \times 10^0 \quad (\text{IV})$$

It computed from the acid number and saponification value by the following formulas (IV).

(2) End carboxyl group concentration: PBT or oligomer 0.5g was dissolved in benzyl alcohol 25mL, and it titrated using 0.01 mols / L benzyl alcohol solution of a sodium hydroxide.

[0195]

(3) Intrinsic viscosity (IV): It asked in the following way using the Ubbelohde viscometer. That is, the mixed solvent of a phenol/tetrachloroethane (weight ratios 1/1) was used, the number of drop seconds of only the concentration of 1.0g / polymer solution of dL, and a solvent was measured in 30 degrees C, and it asked from the following formulas (V).

[0196]

[Equation 5]

$$[\text{IV}] = \left[(1 + 4 \cdot K_H \eta_{sp})^{0.5-1} \right] / (2 \cdot K_H C) \quad (\text{V})$$

[0197]

However, it is eta sp=eta/eta 0-1, and for eta, the number of polymer solution drop seconds and eta 0 are [polymer solution concentration (g/dL) and KH of the number of drop seconds of a solvent and C] the constants of HAGINZU. KH adopted 0.33.

[0198]

(4) Titanium concentration in PBT: Wet degradation of the PBT was carried out with the high grade sulfuric acid for electronic industry, and the nitric acid, and it measured using high-resolution ICP(induced Coupled Plasma)-MS (MassSpectrometer) (thermostat QUEST company make).

[0199]

(5) End methoxycarbonyl group concentration, end vinyl group concentration, and end hydroxyl-group concentration : Heavy chloroform / hexafluoro isopropanol = PBT about 100mg was dissolved in 7/3 (volume

ratio) of mixed solvent 1mL(s), heavy pyridine 36microL was added, and 1 H-NMR was measured and calculated at 50 degrees C. "alpha=400" by JEOL Co., Ltd. or "JNM270" was used for NMR equipment.
 [0200]

(6) Temperature fall crystallization temperature (Tc) :

After using the differential scanning calorimeter [PerkinElmer, Inc. and a type DSC7] and carrying out temperature up from a room temperature to 300 degrees C by the programming rate of 20 degrees C / min, the temperature was lowered to 80 degrees C by 20 degrees C in temperature fall rate / min, and temperature of an exothermic peak was made into temperature fall crystallization temperature. A crystallization rate is so quick that Tc is high, and a molding cycle becomes short.

[0201]

(7) Solution Hayes :

A phenol/tetrachloroethane = after dissolving PBT2.70g in 3/2 (weight ratio) of mixed solvent 20mL(s) for 30 minutes at 110 degrees C, it cooled for 15 minutes with the 30-degree C constant temperature bath, the turbidity meter (NDH-300A) by Nippon Denshoku Co., Ltd. was used, and it measured by 10mm of cel length. It is shown that transparency is so good that a value is low.

[0202]

(8) Pellet color tone :

The color difference meter (Z-300A mold) by Nippon Denshoku Co., Ltd. was used, and the yellow index b value was computed and evaluated. It is shown that there is little yellowish color and a color tone is so good that a value is low.

[0203]

(9) Lifting of the end carboxyl group concentration by the pyrolysis (delta [COOH]) :

After carrying out the vacuum drying of the PBT to the moisture of 300 ppm or less, it heat-treated for 40 minutes with the 245-degree C oil bath among a glass tube and under desiccation nitrogen-gas-atmosphere mind, the end carboxyl group concentration and end hydroxyl-group concentration before and behind heat treatment were measured, and it computed by the above-mentioned formula (I).

[0204]

(10) Tensile strength and whenever [**** breaking extension] :

The injection molding machine (the product made from Sumitomo Heavy machinery: type S-75MII) was used, the ISO test piece of a resin constituent was fabricated with the cylinder temperature of 250 degrees C, and the die temperature of 80 degrees C, and whenever [tensile strength (TS) and **** breaking extension] was measured with them according to ISO527.5 times of the averages were used for each of these.

[0205]

(11) Hydrolysis-proof nature (retention on the strength after a hydrolysis trial) :

After [which cannot touch / the pressurized container which stretched pure water / the same ISO test piece as the above at direct water] putting in like and sealing, it processes under 121-degree C application of pressure for 100 hours, and a tension test is performed like the above (the average of the tensile strength after processing is made into TS'). And retention on the strength is computed by the following formulas (VI). However, in the case of the resin constituent with which moist heat treatment contains a consolidation filler, in the case of the resin constituent which does not contain a consolidation filler, it was made into 60 hours for 100 hours. It is shown that hydrolysis-proof nature is so good that retention on the strength is large.

[0206]

[Equation 6]

$$\text{强度保持率 (\%)} = \frac{(TS' / TS) \times 100}{(TS' / TS) \times 100 + 100} \quad \text{(VI)}$$

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[0207]

(12) The number of foreign matters of 5 micrometers or more in PBT :

Hexafluoro isopropanol / chloroform = after dissolving PBT10g in two thirds of mixed solvents (volume ratio) by 20% of the weight of concentration and filtering with the membrane filter made from polytetrafluoroethylene of 5 micrometers of apertures, the above-mentioned mixed solvent washed enough, and counting of the number of foreign matters which remained on the filter was observed and carried out with the optical microscope.

[0208]

(13) Charpy impact strength :

After performing notch processing to the same ISO test piece as the above, Charpy impact strength was measured according to ISO179.

[0209]

Example 1 :

PBT was manufactured for the polycondensation process shown in the esterification process shown in drawing 1, and drawing 4 in through and the following way. First, to 1.00 mols of terephthalic acids, the reaction vessel (A) for esterification which has the screw mold agitator beforehand filled up with PBT oligomer of 99% of rates of esterification for the 60-degree C slurry mixed at a rate of 1.80 mol of 1,4-butanediol through a slurry preparation tub to the feeding line (1) was continuously supplied so that it might become 28.5 kg/h. Simultaneously, the bottom component of a 185-degree C fractionating tower (C) was supplied by h in 12.0kg / from the recirculation line (2), and the 6.0-% of the weight 1,4-butanediol solution of 65-degree C tetrabutyl titanate was supplied by 69 g/h as a catalyst from the catalyst supply line (3) (it is 30 ppm to theoretical polymer yield). The moisture in this solution was 0.20 % of the weight.

[0210]

Set the internal temperature of a reaction vessel (A) into 230 degrees C, set the pressure to 78kPa(s), the water to generate, a tetrahydrofuran, and excessive 1,4-butanediol were made to distill from a distillate line (5), and it separated into the high-boiling component and the low-boiling component in the fractionating tower (C), 98 % of the weight or more is 1,4-butanediol, and the high-boiling component of the bottom after a system is stabilized extracted the part outside through the extraction line (8) so that the oil level of a fractionating tower (C) might become fixed. On the other hand, the low-boiling component was extracted outside from the extraction line (13) so that it might extract with the gestalt of gas, and might be made to condense by the capacitor (G) and the oil level of a tank (F) might become fixed from the overhead.

[0211]

The constant rate of the oligomer generated by the reaction vessel (A) used the pump (B), extracted it from the extraction line (4), and it controlled the oil level so that the mean flow-time of (reaction-vessel A) inner liquid was set to 3.3hr(s). The oligomer extracted from the extraction line 4 was continuously supplied to the 1st-fold condensation reaction tub (a). After a system was stabilized, the rate of esterification of the oligomer extracted at the outlet of a reaction vessel (A) was 97.6%.

[0212]

The internal temperature of the 1st-fold condensation reaction tub (a) was set to 240 degrees C and pressure 2.1kPa, and liquid level control was performed so that the residence time might become in 120 minutes. The initial polycondensation reaction was performed extracting water, a tetrahydrofuran, and 1,4-butanediol from the vent line (L2) connected to the reduced pressure machine (not shown). Extracted reaction mixture was continuously supplied to the 2nd-fold condensation reaction tub (d).

[0213]

The internal temperature of the 2nd-fold condensation reaction tub (d) was made into 238 degrees C and the pressure of 125Pa, liquid level control was performed so that the residence time might become in 40 minutes, and the polycondensation reaction was advanced further, extracting water, a tetrahydrofuran, and 1,4-butanediol from the vent line (L4) connected to the reduced pressure machine (not shown). The obtained polymer was continuously extracted in the

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shape of a strand from the dice head (g) via the extraction line (L3) with the gear pump for extractions (e), and was cut by the rotating type cutter (h).

[0214]

0.70 dL/g and the end carboxyl group concentration of the intrinsic viscosity of the obtained polymer were 8.3microeq/g. Other analysis values were collectively shown in a table 1. There were few foreign matters and it excelled in the color tone, and transparency was good and PBT excellent in thermal stability or hydrolysis-proof nature was obtained.

[0215]

Example 2 : In the example 1, it carried out like the example 1 except having adopted the polycondensation process shown in drawing 5. As a filter (f) of the polycondensation process shown in drawing 5, the pleat mold cylinder type filter of 20 micrometers of absolute filtration accuracies which consist of a metal nonwoven fabric was used. PBT by which the foreign matter was further reduced from the example 1 was obtained. The analysis value was collectively shown in a table 1.

[0216]

Example 3 : In the example 1, the amount of supply of tetrabutyl titanate was adjusted so that it might become, as Ti content in a polymer was a table 1, and it carried out like the example 1 except having set the pressure of the 2nd-fold condensation reaction tub (d) to 150Pa. There were few foreign matters and it excelled in the color tone, and transparency was good and PBT excellent in thermal stability was obtained. The analysis value was collectively shown in a table 1.

[0217]

Example 4 : In the example 1, the rate of the bottom component of the fractionating tower (C) supplied to a reaction vessel (A) from a recirculation line (2) was changed into 5.6 kg/h, and it carried out like the example 1 except having made the internal temperature of the 2nd-fold condensation reaction tub (d) into 241 degrees C. There were few foreign matters and it excelled in the color tone, and transparency was good and PBT excellent in thermal stability was obtained. The analysis value was collectively shown in a table 1.

[0218]

Example 1 of a comparison :

In the example 1, the catalyst supply line (3) of the esterification process shown in drawing 1 was made to connect with a feeding line (1), the recirculation line (2) was located in the gaseous-phase section of a reaction vessel (A), and it carried out like the example 1 except having carried out the amount of supply of the 1,4-butanediol solution of tetrabutyl titanate in 408g/h, and having set the pressure of the 2nd-fold condensation reaction tub (d) to 200Pa. There were many end carboxyl groups as 23.5microeq/g, Hayes and a color tone got worse and obtained PBT also had many foreign matters. The analysis value was collectively shown in a table 1.

[0219]

Example 2 of a comparison :

272.9 mol [of dimethyl terephthalates] (DMT) and 1,4-butanediol 327.5mol and 0.076 mols (60 ppm per theoretical yield polymer as an amount of titanium) of tetrabutyl titanate were taught to the reaction container made from stainless steel of content volume 200L, possessing a turbine mold stirring aerofil, and the nitrogen purge was enough carried out to it. Then, temperature up of the system is carried out, and the ester exchange reaction was carried out for 2 hours, making the methanol generated with the temperature of 210 degrees C, and the bottom atmospheric pressure of nitrogen after 80 minutes, 1,4-butanediol, and a tetrahydrofuran distill out of a system (reaction start time was considered as the event of reaching predetermined temperature and a predetermined pressure).

[0220]

After transporting the oligomer obtained above to the reactor made from stainless steel of content volume 200L which has a vent pipe and a double helical-type stirring aerofil, it was

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made to reach over 60 minutes to the temperature of 240 degrees C, and the pressure of 100Pa, and the polycondensation reaction was performed to it for 1.5 hours with the condition. The polymer was extracted in the shape of a strand after reaction termination, and it cut to the pellet type. 0.70 dL/g and end carboxyl group concentration were as high as 22.0microeq/g. IV of the obtained polymer was inferior also to thermal stability, and its Tc was also low. The analysis value was collectively shown in a table 1.

[0221]

[A table 1]

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made to reach over 60 minutes to the temperature of 240 degrees C, and the pressure of 100Pa, and the polycondensation reaction was performed to it for 1.5 hours with the condition. The polymer was extracted in the shape of a strand after reaction termination, and it cut to the pellet type. 0.70 dL/g and end carboxyl group concentration were as high as 22.0microeq/g. IV of the obtained polymer was inferior also to thermal stability, and its Tc was also low. The analysis value was collectively shown in a table 1.

[0222]

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made to reach over 60 minutes to the temperature of 240 degrees C, and the pressure of 100Pa, and the polycondensation reaction was performed to it for 1.5 hours with the condition. The polymer was extracted in the shape of a strand after reaction termination, and it cut to the pellet type. 0.70 dL/g and end carboxyl group concentration were as high as 22.0microeq/g. IV of the obtained polymer was inferior also to thermal stability, and its Tc was also low. The analysis value was collectively shown in a table 1.

[0223]

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made to reach over 60 minutes to the temperature of 240 degrees C, and the pressure of 100Pa, and the polycondensation reaction was performed to it for 1.5 hours with the condition. The polymer was extracted in the shape of a strand after reaction termination, and it cut to the pellet type. 0.70 dL/g and end carboxyl group concentration were as high as 22.0microeq/g. IV of the obtained polymer was inferior also to thermal stability, and its Tc was also low. The analysis value was collectively shown in a table 1.

[0224]

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項目	単位	実施例1	実施例2	実施例3	実施例4	比較例1	比較例2
B/T	mol/mol	3.35	3.35	3.35	2.52	3.35	1.20
Ti含有量	ppm	30	30	60	30	180	60
UV	dL/g	0.70	0.70	0.70	0.70	0.70	0.70
未端カルボキシ基濃度	μeq/g	8.3	8.3	12.5	7.4	23.5	22.0
Tc	℃	178.8	178.8	179.5	180.3	181.0	169.5
未端カルボキシ基濃度	μeq/g	3.1	3.1	3.3	4.2	4.4	5.5
溶媒Haze	%	0.3	0.3	0.1以下	0.1以下	0.1以下	3.3
Δ[COOH]	μeq/g(40分)	5.9	5.9	9.6	4.2	12.0	10.5
ペレットb値		-1.9	-1.9	-1.3	-1.3	1.8	-0.6
加水分解試験後の強度保持率	%	8.2	8.4	7.3	8.8	3.9	4.0
5μm以上異物数	個/10g	9	4	23	20	7.6	1.3

[0222]

They are the examples 3 and 14 (hydrolysis-proof nature PBT constituent) of a comparison to an example 5 – 9 lists. : every of an example 1, an example 3, the example 1 of a comparison, and the example 2 of a comparison — the pellet 100 weight section of PBT, the component of the following (1) – (3) was blended by the presentation of (2) — the presentation of a table 2 and a table 3 — blending — Twin screw extruder with vent of 30mm of diameters of screw [— by Japan Steel Works:TEX30C], melting kneading was carried out on condition that the temperature of 260 degrees C, and screw-speed 200rpm, and it extruded in the shape of a strand, and pelletized. And assessment shown in a table 2 and a table 3 is performed, and a result is shown in this table.

[0223]

(1) Diglycidyl ether of bisphenol A (the product made from Asahi Electrification, trade name:ADEKA sizer EP-17)
(2) Glass fiber (Nippon Electric Glass [Co., Ltd.] make: the brand name T-187, the diameter of 13 micrometers, fiber length of 3mm)

[0224]

The ISO test piece was fabricated from the above-mentioned pellet, and hydrolysis-proof nature was evaluated. Moreover, the mold-release characteristic was also evaluated. These results are shown in a table 2 and a table 3.

[0225]

[A table 2]

		実施例				
		5	6	7	8	9
配合組成 (重量部)	実施例 1-PBT	100	100	100	100	—
	実施例 3-PBT	—	—	—	—	100
	比較例 1-PBT	—	—	—	—	—
	比較例 2-PBT	—	—	—	—	—
	ガラス繊維	43	18	43	—	43
	エポキシ化合物	0.43	0.35	0.86	0.30	0.43
ペレット b 値		7.2	6.6	9.5	2.9	7.9
耐加水 分解性	引張強度 : MPa	148	97	149	51	146
	湿熱処理前	92	60	100	37	85
	湿熱処理後	62	62	67	73	58
強度保持率 (%)		62	62	67	73	58

[0226]

[A table 3]

		比較例	
		3	4
配合組成 (重量部)	実施例 1-PBT	—	—
	実施例 3-PBT	—	—
	比較例 1-PBT	100	—
	比較例 2-PBT	—	100
	ガラス繊維	43	43
	エポキシ化合物	0.43	0.43
ペレット b 値		11.9	10.7
耐加水 分解性	引張強度 : MPa	147	148
	湿熱処理前	56	55
	湿熱処理後	38	37

[0227]

By blending a consolidation system filler (glass fiber) and an epoxy compound with PBT of an example, b value of a pellet was held down low and, moreover, the consolidation system PBT constituent excellent in hydrolysis-proof nature was able to be obtained as shown in a table 2 and a table 3.

[0228]

They are the examples 5 and 6 (shock-proof PBT constituent) of a comparison to an example 10 – 14 lists. :

every of an example 1, an example 3, and the example 1 of a comparison — to the pellet 100 weight section of PBT, the component of the following (1) – (3) was blended by the presentation of a table 4 and a table 5, and it pelletized by the same approach as an example 5.

[0229]

(1) Diglycidyl ether of bisphenol A (it is the same as having used it in the example 5)

(2) Acrylic rubber (chemical name: an acrylic acid alkyl methacrylate copolymerization object, the Kureha Chemical Industry Co., Ltd. make, trade name:KUREHA Palaloid EXL2315)

(3) Glass fiber (it is the same as having used it in the example 5)

[0230]

The ISO test piece was produced with the injection molding machine from the above-mentioned pellet, and tensile strength, flexural strength, a bending elastic modulus, and Charpy impact value were measured. Moreover, hydrolysis-proof nature was evaluated. A result is shown in a table 4 and a table 5.

[0231]

[A table 4]

		実施例				
		10	11	12	13	14
配合組成 (重量部)	実施例 1-PBT	100	100	100	100	—
	実施例 3-PBT	—	—	—	—	100
	比較例 1-PBT	—	—	—	—	—
	アクリルゴム	16.8	7.8	27.5	15.0	16.8
	ガラス繊維	50.6	46.5	55.0	—	50.6
	エポキシ化合物	0.84	0.78	0.92	0.35	0.84
引張破断伸度		3.9	3.5	4.3	37.0	3.7
冲击 - 衝撃強度		11.3	9.9	12.5	5.2	11.1
耐加水 分解性	引張強度 : MPa	105	123	95	42	104
	湿熱処理前	66	75	62	30	59
	湿熱処理後	63	61	65	71	57

[0232]

[A table 5]

		比較例	
		5	6
配合組成 (重量部)	実施例 1-PBT	-	-
	実施例 3-PBT	-	-
	比較例 1-PBT	100	100
	アクリルゴム	16.8	-
	ガラス繊維	50.6	43.2
	エボキシ化合物	0.84	0.72
	引張破断伸度	%	3.5 2.7
冲击 - 衝撃強度		KJ/m	10.2 9.1
耐加水 分解性	引張強度 : MPa	湿熱処理前	101 134
		湿熱処理後	37 51
	強度保持率 (%)		37 38

[0233]

The PBT constituent excellent in Charpy reinforcement and hydrolysis-proof nature was able to be obtained whenever [**** breaking extension] by making PBT of an example contain a shock-resistant amelioration agent (acrylic rubber), a consolidation filler (glass fiber), and an epoxy compound as shown in a table 4 and a table 5.

[0234]

They are the examples 7 and 8 (fire-resistant PBT constituent) of a comparison to an example 15 - 17 lists.:

every of an example 1, the example 1 of a comparison, and the example 2 of a comparison — to the pellet 100 weight section of PBT, the component of the following (1) - (4) was blended by the presentation of a table 6, and it pelletized by the same approach as an example 5.

[0235]

(1) Bromination aromatic compound : Pori (pen TABUROMO benzyl acrylate) (a BUROMOKEMU Far East company, trade name=BBPA-FR1025)

(2) Antimony trioxide (made in six companies of woods)

(3) Polytetrafluoroethylene (PTFE) (the Daikin Industries, LTD. make, trade name:Pori Flon FA-500)

(4) Glass fiber (it is the same as having used it in the example 5)

[0236]

UL-94 test piece (1/32 inch thickness) was fabricated from the above-mentioned pellet, and the inflammable trial was performed according to UL-94. UL-94 test piece was fabricated with the

(4) Cyanuric acid melamine (Mitsubishi Chemical make)

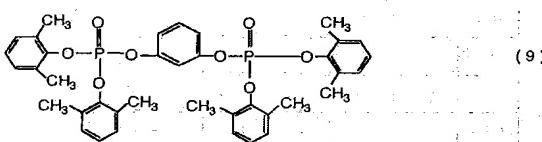
(5) Glass fiber (it is the same as having used it in the example 5)

(6) Polytetrafluoroethylene (PTFE) (the Daikin Industries, LTD. make, trade name:Pori Flon FA-500)

(7) Zinc borate (made in borax Japan, trade name:Firebreak ZB)

[0241]

[Formula 9]



[0242]

UL-94 test piece (1/32 inch thickness) was fabricated from the above-mentioned pellet, and the inflammable trial was performed according to UL-94. UL-94 test piece was fabricated with the cylinder temperature of 270 degrees C, and the die temperature of 80 degrees C with the injection molding machine (Japan Steel Works make: type J28SA). Moreover, the ISO test piece for tensile test was fabricated from the above-mentioned pellet, and hydrolysis-proof nature was evaluated. These results are shown in a table 7 and a table 8.

[0243]

[A table 7]

cylinder temperature of 270 degrees C, and the die temperature of 80 degrees C with the injection molding machine (Japan Steel Works make: type J28SA). Moreover, the ISO test piece for tensile test was fabricated from the above-mentioned pellet, and hydrolysis-proof nature was evaluated. These results were indicated to a table 6.

[0237]

[A table 6]

		実施例		比較例			
		15	16	17	7	8	
配合組成 (重量部)	実施例 1-PBT	100	100	100	-	-	
	比較例 1-PBT	-	-	-	100	-	
	P B B P A	15.4	12.6	13.0	12.6	12.6	
	三酸化 ナフチル	7.7	4.4	5.0	4.4	4.4	
	P T F E	1.0	3.0	0.5	3.0	3.0	
	ガラス繊維	53.2	51.4	-	51.4	51.4	
	難燃性	UL-94	V-0	V-0	V-0	V-0	
耐加水 分解性	引張強度 : MPa	湿熱処理前	132	131	41	131	130
		湿熱処理後	70	68	29	54	55
	強度保持率 (%)		53	52	71	41	42

[0238]

The PBT constituent excellent in fire retardancy and hydrolysis-proof nature was able to be obtained by blending a bromination aromatic compound flame retarder (PBBPA), an antimony compound (antimony trioxide), a dropping inhibitor (PTFE), and a consolidation filler (glass fiber) with PBT of an example as shown in a table 6.

[0239]

They are the examples 9 and 10 (non-halogen fire retardancy PBT constituent) of a comparison to an example 18 - 21 lists.:

The component of the following (1) - (7) was blended with each PBT100 weight section of an example 1, the example 1 of a comparison, and the example 2 of a comparison by the presentation of a table 7 and a table 8, and it pelletized by the same approach as an example 5.

[0240]

(1) Polyphenylene ether (PPE) (the product made from Mitsubishi Engineering plastics, a trade name lupiace (trademark), intrinsic viscosity 0.36)

(2) Polycarbonate resin (PC) (grade [the product made from Mitsubishi Engineering plastics, a trade name "nova REXX" (trademark), and] 7022PJ, viscosity average molecular weight: about 21000)

(3) Phosphoric ester shown by the bottom formula (8)

		実施例				
		18	19	20	21	
配合組成 (重量部)	実施例 1-PBT	70	70	70	80	
	比較例 1-PBT	-	-	-	-	
	比較例 2-PBT	-	-	-	-	
	P P E	30	30	30	20	
	P. C	2	2	2	2	
	リチウム ベニミン	15	20	15	20	
	ジフェニル ベニミン	15	20	15	20	
難燃性	ガラス繊維	59	62	-	-	
	P T F E	1	0.5	1	-	
	硼酸亜鉛	4	1	4	-	
耐加水 分解性	UL-94	V-0	V-0	V-0	V-0	
	引張強度 : MPa	湿熱処理前	102	100	44	40
		湿熱処理後	53	51	28	24
	強度保持率 (%)		52	51	64	60

[0244]
[A table 8]

		比較例	
		9	10
配合組成(重量部)	実施例 1-PBT	-	-
	比較例 1-PBT	70	-
	比較例 2-PBT	-	70
	P P E	30	30
	P C	2	2
	リン酸エスカル	15	15
	シリカ酸ラミン	15	15
	ガラス繊維	59	59
	P T F E	1	1
	硼酸亜鉛	4	4
難燃性	UL-9-4	V-0	V-0
耐加水 分解性	引張強度 : MPa	湿熱処理前	100
		湿熱処理後	35
	強度保持率 (%)	35	36

[0245]

The PBT constituent which was excellent in PBT and polyphenylene ether resin of an example at fire retardancy and hydrolysis-proof nature by blending a compatibilizer (polycarbonate), phosphoric ester, a cyanuric acid melamine, a consolidation filler (glass fiber), a dropping inhibitor (PTFE), and a boric acid metal salt was able to be obtained as shown in a table 7 and a table 8.

[Brief Description of the Drawings]

[0246]

[Drawing 1] The explanatory view of an example of the esterification reaction process adopted by this invention, or an ester exchange reaction process

[Drawing 2] The explanatory view of other examples of the esterification reaction process adopted by this invention, or an ester exchange reaction process

[Drawing 3] The explanatory view of other examples of the esterification reaction process adopted by this invention, or an ester exchange reaction process

[Drawing 4] The explanatory view of an example of the polycondensation process adopted by

this invention

[Drawing 5] The explanatory view of other examples of the polycondensation process adopted by this invention

[Drawing 6] The explanatory view of other examples of the polycondensation process adopted by this invention

[Drawing 7] The explanatory view of other examples of the polycondensation process adopted by this invention

[Description of Notations]

[0247]

1: Feeding line

2: Recirculation line

3: Catalyst supply line

4: Extraction line

5: Distillate line

6: Extraction line

7: Circulation line

8: Extraction line

9: Mold-gassing appearance line

10: Condensate line

11: Extraction line

12: Circulation line

13: Extraction line

14: Vent line

15: Recovery line

16: Bypass line

A: Reaction vessel

B: Extraction pump

C: Fractionating tower

D, E: Pump

F: Tank

G: Capacitor

H: Reboiler

L1: Extraction line

L3, L5: Extraction line

L2, L4, L6: Vent line

a: The 1st-fold condensation reaction tub

d: The 2nd-fold condensation reaction tub

k: The 3rd-fold condensation reaction tub

c, e, m: The gear pump for extractions

f: Filter

g: Dice head

h: Rotating type cutter

[Translation done.]

* NOTICES *

JPO and NCIP are not responsible for any
damages caused by the use of this translation.

- 1.This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.**** shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[0246]

[Drawing 1] The explanatory view of an example of the esterification reaction process adopted by this invention, or an ester exchange reaction process

[Drawing 2] The explanatory view of other examples of the esterification reaction process adopted by this invention, or an ester exchange reaction process

[Drawing 3] The explanatory view of other examples of the esterification reaction process adopted by this invention, or an ester exchange reaction process

[Drawing 4] The explanatory view of an example of the polycondensation process adopted by this invention

[Drawing 5] The explanatory view of other examples of the polycondensation process adopted by this invention

[Drawing 6] The explanatory view of other examples of the polycondensation process adopted by this invention

[Drawing 7] The explanatory view of other examples of the polycondensation process adopted by this invention

[Translation done.]